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ARTICLES HAVING A PHOTOCHROMIC POLYMERIC COATING

Abstract:

14b1 Abstract of WO03037998

Described is a photochromic article that includes a substrate and at least a partial coating of an at least partially cured polymerizable composition of a photochromic amount of at least one photochromic compound, at least one material having at least one carbonate group and at least one hydroxyl group, and at least one monoisocyanate containing material having at least one unsaturated group. Also described are photochromic optical elements such as ophthalmic lenses, prepared from an optical element substrate coated with the photochromic polymerizable composition. Data supplied from the esp@cenet database - Worldwide

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(54) Title: ARTICLES HAVING A PHOTOCHROMIC POLYMERIC COATING

(57) Abstract: Described is a photochromic article that includes a substrate and at least a partial coating of an at least partially cured polymerizable composition of a photochromic amount of at least one photochromic compound, at least one material having at least one carbonate group and at least one hydroxyl group, and at least one monoisocyanate containing material having at least one unsaturated group. Also described are photochromic optical elements such as ophthalmic lenses, prepared from an optical element substrate coated with the photochromic polymerizable composition.



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## ARTICLES HAVING A PHOTOCHROMIC POLYMERIC COATING

Cross Reference to Related Applications

This application claims priority to provisional  
5 application Serial No. 60/335,871 filed November 1, 2001.

BACKGROUND OF THE INVENTION

The present invention relates to photochromic articles comprising a substrate having at least a partial coating of an at  
10 least partially cured coating of a photochromic polymerizable composition. Photochromic compounds can be added to the composition prior to polymerization or after an at least partially cured coating is formed. The present invention also relates to photochromic articles that are optical elements having at least a partial coating  
15 of an at least partially cured coating of a photochromic polymerizable composition.

Photochromism is a phenomenon involving a reversible change in color of a photochromic compound, or an article containing such a compound, upon exposure to light radiation containing  
20 ultraviolet rays, and a reversion to the original color when the influence of the ultraviolet radiation is discontinued. Sources of light radiation that contain ultraviolet rays include, for example, sunlight and the light of a mercury lamp. Discontinuation of the ultraviolet radiation can be achieved for example by storing the  
25 photochromic compound or article in the dark or by removing the source of ultraviolet radiation (e.g., by means of filtering).

The general mechanism responsible for the reversible change in color, i.e., a change in the absorption spectrum in the visible range of light (400-700 nm), exhibited by different types  
30 of photochromic compounds has been described and categorized. See John C. Crano, "Chromogenic Materials (Photochromic)", Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, 1993, pp. 321-332. The general mechanism for the most common classes of  
35 photochromic compounds, e.g., indolino spiropyrans and indolino spirooxazines, involves an electrocyclic mechanism. When exposed to activating radiation, these compounds transform from a colorless closed ring compound into a colored open ring species. In contrast, the colored form of fulgide photochromic compounds is

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produced by an electrocyclic mechanism involving the transformation of a colorless open ring form into a colored closed ring form.

In the aforescribed electrocyclic mechanisms, the photochromic compounds require an environment in which they can reversibly transform. In solid polymer matrices, the rates at which the photochromic processes of activation, i.e., formation of color or darkening, and fading, i.e., the return to the original or colorless state, occur are believed to be dependent on the free volume in the polymer matrix. The free volume of the polymer matrix is dependent upon the flexibility of the chain segments of the polymer environment surrounding the photochromic compound, i.e., the local mobility or local viscosity of the chain segments comprising the matrix. See Claus D. Eisenbach, "New Aspects of Photochromism in Bulk Polymers", Photographic Science and Engineering, 1979, pp. 183-190. One of the main obstacles reported by Claus D. Eisenbach, for the larger commercial application of photochromic systems, is the slow rate of photochromic activation and fade in a solid polymer matrix.

Recently, photochromic plastic materials have been the subject of considerable attention in part due to the weight advantage that they can offer relative to ophthalmic lenses made of glass. In addition, photochromic transparencies for vehicles, such as automobiles and airplanes, have been of interest because of the potential safety features that such transparencies offer.

In addition to the slow rate of activation and fade of photochromic compounds in polymer matrices, a further drawback to the widespread commercial use of organic photochromic compounds in combination with plastic materials is the loss of their ability to exhibit a reversible change in color as a result of prolonged repeated exposure to ultraviolet (UV) light. This phenomenon is believed to be a result of irreversible decomposition of the organic photochromic compound and is referred to as fatigue.

While some advancements have been made toward increasing the fatigue resistance and improving the performance of photochromic materials, further improvements, even small incremental improvements, in the fatigue resistance and/or improving the performance of photochromic polymeric materials are

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still required. Hence, efforts to obtain such improvements have continued.

Although the use of photochromic compounds in combination with polymerizable compositions, e.g., (meth)acrylates, is known, the use of the polymerizable composition of the present invention with photochromic compounds as at least a partial coating of an at least partially cured coating on a substrate has not been disclosed.

10                    DETAILED DESCRIPTION OF THE INVENTION

          In one non-limiting embodiment of the present invention, there is provided a photochromic article comprising a substrate having at least a partial coating of an at least partially cured coating of a polymerizable composition comprising a photochromic amount of at least one photochromic compound, at least one material having at least one carbonate group and at least one hydroxyl group and at least one monoisocyanate containing material having at least one unsaturated group. This composition can optionally contain other copolymerizable monomers.

20            In a further non-limiting embodiment, the photochromic article of the present invention is adapted to provide a reduction in the percent photopic fatigue of the photochromic compound in the Accelerated Weathering Photochromic Percent Photopic Fatigue Test (AWPPPF Test). The AWPPPF Test is described in Example 15 herein. In the test, lenses coated with the photochromic polymerizable composition of the present invention and other polymerizable compositions are tested for photochromic performance and fatigue as components of a methacrylic coating composition.

          In another non-limiting embodiment of the present invention, there is provided a photochromic article comprising a substrate having at least a partial coating of an at least partially cured coating of a polymerizable composition comprising component (a) a reaction product of a polyol comprising at least one carbonate group and an isocyanate comprising one reactive isocyanate group and at least one polymerizable double bond; and optionally component (b) at least one other monomer copolymerizable with component (a) and component (c) a photochromic amount of at least one photochromic compound.

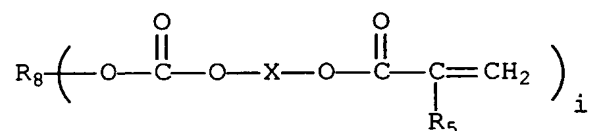
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In one non-limiting embodiment, it has unexpectedly been found that the photochromic article of the present invention demonstrates a reduction in the Percent Fatigue of the photochromic compound as described in the AWPPPF Test described in Example 15, herein. It has also been found that the photochromic article of the present invention demonstrated in the aforementioned AWPPPF test, a lower amount of Percent Fatigue of the photochromic compound as compared to a photochromic article coated with a methacrylic coating containing a polycarbonate based dimethacrylate monomer without a urethane group.

In the various non-limiting embodiments of the photochromic polymerizable composition used to produce the photochromic article of the present invention, the exact nature of optional component (b) is not critical other than that it is copolymerizable with the photochromic polymerizable composition. Any copolymerizable monomer can be used.

In one non-limiting embodiment, the copolymerizable monomers of component (b) can be chosen from:

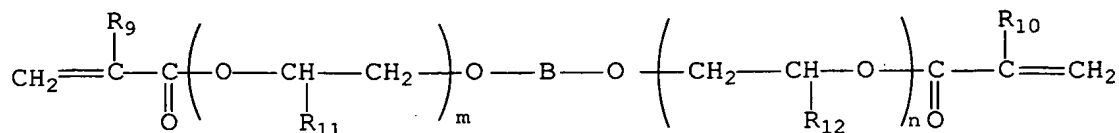
(a) a radically polymerizable monomer represented by the following formula:



wherein  $R_8$  is a polyvalent residue of a polyol,  $R_5$  is hydrogen or methyl,  $i$  is chosen from an integer from 2 to 6, and  $X$  is a divalent linking group chosen from linear or branched chain alkylene, linear or branched chain polyoxyalkylene, cyclic alkylene, phenylene, residue of a polyol or a  $C_1$ - $C_4$  alkyl substituted phenylene;

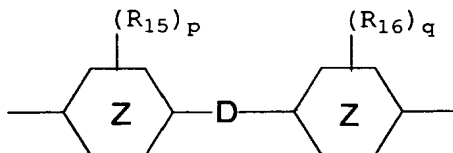
(b) a radically polymerizable monomer represented by the following formula:

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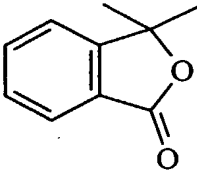

wherein m and n are each independently chosen from an integer from 0 to 6, the sum of m and n being from 0 to 6,  $R_9$  and  $R_{10}$  are each independently chosen from hydrogen or methyl,  $R_{11}$  and  $R_{12}$  are each independently chosen for each occurrence from hydrogen or  $C_1$  to  $C_4$  alkyl, and B is a divalent linking group chosen from linear or branched chain alkylene, phenylene,  $C_1$ - $C_9$  alkyl substituted phenylene, or a group represented by the following formula:




wherein  $R_{15}$  and  $R_{16}$  are each independently chosen for each occurrence from  $C_1$ - $C_4$  alkyl, chlorine or bromine, p and q are each



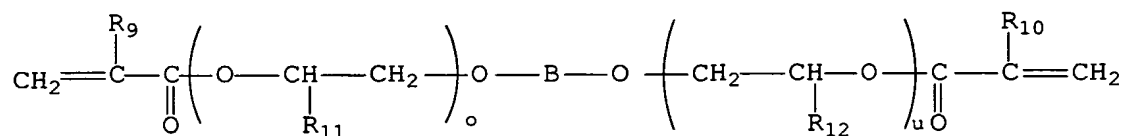
independently chosen from an integer from 0 to 4, represents a divalent benzene group or a divalent cyclohexane group and D is  $-O-$ ,  $-S-$ ,  $-S(O_2)-$ ,  $-C(O)-$ ,  $-CH_2-$ ,  $-CH=CH-$ ,  $-C(CH_3)_2-$ ,  $-C(CH_3)(C_6H_5)-$ , or

15  when  is the divalent benzene group, and D

is  $-O-$ ,  $-S-$ ,  $-CH_2-$ , or  $-C(CH_3)_2-$  when  is the divalent cyclohexane group;

(c) a radically polymerizable monomer represented by the following formula:

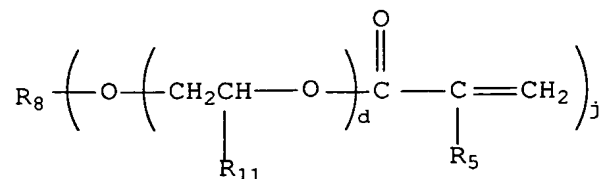
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wherein o and u are each independently chosen from a positive number, the sum of o and u being from 7 to 70,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$ , and B are the same as defined hereinbefore;

(d) a radically polymerizable monomer represented by the following formula:



wherein  $R_5$ ,  $R_8$  and  $R_{11}$  are the same as defined hereinbefore, d is chosen from a number from 0 to 20, and j is chosen from a number from 3 to 6;

(e) a reaction product of a polycarbonate polyol polychloroformate and a hydroxy(meth)acrylate;

(f) a reaction product of a polycarbonate polyol and (meth)acryloyl chloride;

(g) a radically polymerizable monomer that is monoethylenically unsaturated;

(h) a radically polymerizable monomer that is an allyl functional monomer having at least two allyl groups provided that said allyl functional monomer is used at a level that does not exceed 5 weight percent, based on the total weight of the monomers; or

(i) a mixture thereof.

In various non-limiting embodiments, the photochromic compounds can be added prior to polymerization of the polymerizable composition, to an at least partially cured coating or by a combination of such methods to produce the photochromic articles of the present invention.

It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of

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ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the

5 following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at

10 least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific

15 examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

The phrase "at least a partial coating" means an amount

20 of coating covering from a portion to the complete surface of the substrate. The phrase "an at least partially cured polymerizate" refers to a polymerizable composition in which the curable or cross-linkable components are at least partially cured, crosslinked and/or reacted. In certain non-limiting embodiments

25 of the present invention, the degree of reacted components can vary widely, e.g., from 5% to 100% of all of the possible curable, crosslinkable and/or reactable components.

The disclosure of the related applications, patents and articles listed by column and line number or specific citation

30 herein which describe methods for preparing monomers, polymerizates and photochromic compounds are incorporated herein, *in toto*, by reference.

The term "polyol" is defined herein as a polyhydric alcohol having 2 or more hydroxyl groups, but is substantially

35 free of carbonate groups unless indicated otherwise. A residue of a polyol or a radical derived from a polyol is what remains after removal of the hydroxyl group(s) from the polyol. The term "alkylene", when preceded by linear, i.e., straight, or branched

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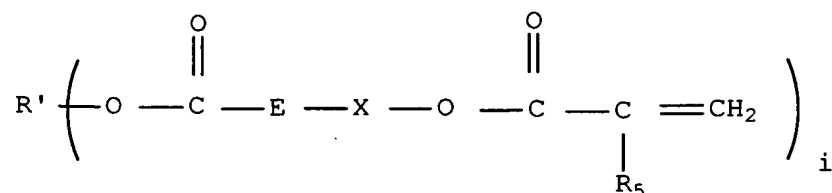
chain, is defined herein as a hydrocarbon group having from 2 to 20 carbon atoms. The term "oxyalkylene" is defined herein as a hydrocarbon group having from 2 to 4 carbon atoms and 1 oxygen atom. Regarding "oxyalkylene groups", it is defined herein that 5 the number of oxyalkylene included in formulas and described, for example as being an integer or number between 0 and 6, that partial numbers such as 1.1 or 5.9 are included within the range specified. The term "cyclic alkylene" is defined herein as a cyclic hydrocarbon group having from 3 to 7 carbon atoms. The 10 term "(meth)acryloyl" is defined as acryloyl groups, methacryloyl groups, or combinations of acryloyl and methacryloyl groups. The term "(meth)acrylate" is defined here as acrylates, methacrylates or combinations of acrylates and methacrylates. The term "(meth)acrylic" is defined here as acrylic, methacrylic or 15 combinations of acrylic and methacrylic groups.

In the descriptions of components (a) and (b), like letters and like terms have the same meaning unless stated otherwise.

The photochromic articles of the present invention 20 comprise a substrate and at least a partial coating of an at least partially cured photochromic polymerizable composition. In one non-limiting embodiment, the photochromic polymerizable composition is the reaction product of: at least one material comprising at least one carbonate group and at least one hydroxyl 25 group, such as a carbonate group containing alcohol or polyol or a (meth)acrylic monomeric material containing at least one carbonate and at least one hydroxyl group; at least one monoisocyanate containing material having at least one unsaturated group, such as the reaction product of an (meth)acrylic monomeric material 30 containing a vinyl ether group and isocyanic acid; and a photochromic amount of at least one photochromic compound.

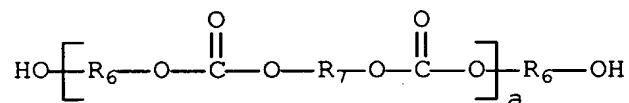
In another non-limiting embodiment, component (a) being the reaction product of an isocyanate comprising one reactive isocyanate group and at least one polymerizable double bond and a 35 polyol comprising at least one carbonate group can be represented by the following formula:

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wherein R' is a residue of a polyol comprising at least one carbonate group, R<sub>5</sub> is hydrogen or methyl, E is -NH-; X is a divalent linking chosen from linear or branched chain alkylene, linear or branched chain polyoxyalkylene, cyclic alkylene, phenylene, residue of a polyol or C<sub>1</sub>-C<sub>4</sub> alkyl substituted phenylene, and i is an integer from 2 to 6. In another non-limiting embodiment, R' is a residue of a polyol comprising at least two carbonate groups.

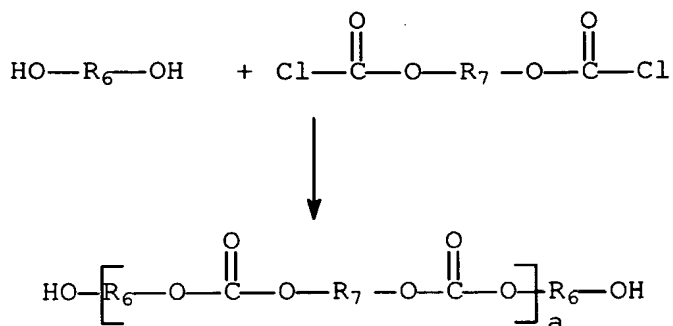
10 In one non-limiting embodiment, the polycarbonate polyol of component (a) can be represented by the following formula:



wherein R<sub>6</sub> and R<sub>7</sub> can be the same or different and are each independently chosen for each occurrence from divalent linear or branched alkylene groups, cyclic alkylene groups or divalent C<sub>6</sub>-C<sub>15</sub> aromatic radicals, e.g. 2,2-diphenylenepropane, and a is an integer from 1 to 20.

In another non-limiting embodiment, the polycarbonate polyols of the aforementioned formula can be formed by the reaction of at least one bis(chloroformate) with at least one polyol, e.g., a diol, as described in U.S. Patent 5,266,551. One of the components can be used in excess to limit and control the molecular weight of the resulting polycarbonate polyol. As shown in the following non-limiting illustration of a Polycarbonate Preparation Scheme, the diol is in excess and becomes the end group.

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Polycarbonate Preparation Scheme

5                Examples of bis(chloroformates) which can be used in the  
 the aforescribed preparation scheme include, but are not limited  
 to: monoethylene glycol bis(chloroformate), diethylene glycol  
 bis(chloroformate), propanediol bis(chloroformate), butanediol  
 bis(chloroformate), hexanediol bis(chloroformate), neopentyl diol  
 10 bis(chloroformate), bisphenol A bis(chloroformate) or a mixture  
 thereof.

              Examples of polyols which can be used in the  
 aforescribed preparation scheme include, but are not limited to:  
 bisphenol A; trimethylolethane; trimethylolpropane; di-  
 15 (trimethylolpropane)dimethylol propionic acid; ethylene glycol;  
 propylene glycol; 1,3-propanediol; 2,2-dimethyl-1,3-propanediol;  
 1,2-butanediol; 1,4-butanediol; 1,3-butanediol; 1,5-pentanediol;  
 2,4-pentanediol; 2,2,4-trimethyl-1,3-pentanediol; 2-methyl-1,3-  
 pentanediol; 2-methyl-1,5-pentanediol; 3-methyl-1,5-pentanediol;  
 20 1,6-hexanediol; 2,5-hexanediol; 2-ethyl-1,3-hexanediol; 1,4-  
 cyclohexanediol; 1,7-heptanediol; 2,4-heptanediol; 1,8-octanediol;  
 1,9-nonanediol; 1,10-decanediol;; 2,2-dimethyl-3-hydroxypropyl-  
 2,2-dimethyl-3-hydroxypropionate; diethylene glycol; triethylene  
 glycol; tetraethylene glycol; polyethylene glycol; dipropylene  
 25 glycol; tripropylene glycol; polypropylene glycol; 1,4-  
 cyclohexanedimethanol; 1,2-bis(hydroxymethyl)cyclohexane; 1,2-  
 bis(hydroxyethyl)cyclohexane; the alkoxylation product of 1 mole  
 of 2,2-bis(4-hydroxyphenyl)propane (i.e., bisphenol-A) and from 2  
 to 10 moles of ethylene oxide, propylene oxide or a mixture  
 30 thereof; poly(oxytetramethylene)diols or a mixture thereof.

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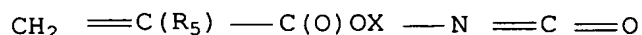
In some non-limiting embodiments, the above materials can be combined to form a variety of compositions, chain lengths and end groups for a polycarbonate polyol. For example, the polyols can have terminal aliphatic hydroxyl groups (e.g.,  
5 diethylene glycol groups), phenolic terminal groups (e.g., bisphenol A groups) or a mixture of such terminal hydroxyl groups.

In various non-limiting embodiments, the polycarbonate polyols as well as the materials containing at least one carbonate group and at least one hydroxyl group can be prepared by an ester  
10 interchange reaction of a dialkyl, diaryl or alkylene carbonate with a polyol, as described in U.S. Patents 4,131,731, 4,160,853, 4,891,421 and 5,143,997. Other examples of such carbonate and hydroxyl group containing materials include products prepared: by the reaction of a polyol and phosgene, as described in U.S. Patent  
15 4,533,729; and by the reaction of a polycarbonate polyol with an acid anhydride or a dicarboxylic acid, as described in U.S. Patent 5,527,879. Examples of commercially available products include but are not limited to: RAVECARB® 102-108 series of polycarbonate diols available from EniChem Synthesis Milano and PC 1122  
20 available from Stahl USA.

In one non-limiting embodiment, the monoisocyanate used to produce the photochromic polymerizable composition has a primary, secondary or tertiary isocyanate group, which is also referred to as a reactive isocyanate group, and at least one  
25 unsaturated group chosen from allylic, (meth)acrylic, vinyl or a mixture thereof. In another non-limiting embodiment, the unsaturated group is a group having a polymerizable double bond chosen from the (meth)acrylic group.

In a series of non-limiting embodiments, the isocyanate  
30 of component (a) as well as the monoisocyanate material containing at least one unsaturated group can be:

(1) an isocyanate represented by the following formula:



35 wherein  $\text{R}_5$  and X are the same as previously described;

(2) m-isopropenyl- $\alpha$ ,  $\alpha$ -dimethyl benzyl isocyanate;

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(3) a product of the reaction of at least one acrylic functional monomer containing a vinyl ether group and isocyanic acid; or

(4) a mixture thereof.

5 In one non-limiting embodiment, isocyanates that can be used as reactants to form component (a) are materials that have one reactive isocyanate group and at least one polymerizable double bond. A non-limiting example of such a compound is isocyanatoethylmethacrylate. By way of non-limiting illustration,  
10 methods for preparation of such a compound have been disclosed by Thomas, Mary R., in "Isocyanatoethyl Methacrylate: A Heterofunctional Monomer for Polyurethane and Vinyl Polymer Systems", Organic Coatings and Polymer Science Proceedings, Volume 46, pp. 506-513, 1982. Non-limiting methods for preparation of m-  
15 isopropenyl- $\alpha$ ,  $\alpha$ -dimethyl benzyl isocyanate are disclosed in U.S. Patents 4,377,530; 4,379,767; and 4,439,616. By way of further non-limiting illustration, methods for preparation of a product of the reaction of an acrylic functional monomer containing a vinyl ether group and isocyanic acid, e.g., 1-(2-  
20 methacryloxyethoxy)ethyl isocyanate, have been disclosed by Hoover, F. W., et al., in "Chemistry of Isocyanic Acid. II. Reaction with  $\alpha$ ,  $\beta$ -Unsaturated Ethers", Journal of Organic Chemistry, Volume 28, pp. 2082 - 2085, 1963.

In further non-limiting embodiments, the isocyanates of  
25 component (a), as defined herein, can include "modified" or "unmodified" isocyanates having "free", "blocked" or partially blocked isocyanate groups. The isocyanate-containing compounds can be chosen from aliphatic, aromatic, cycloaliphatic, heterocyclic isocyanates or a mixture thereof. The term  
30 "modified" is defined herein to mean that the aforementioned isocyanate-containing compounds are changed in a known manner to introduce biuret, urea, carbodiimide, urethane or isocyanurate groups. Other methods for modifying the isocyanates are described in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition,  
35 1989, Vol. A14, pages 611 to 625, and in U.S. Patent 4,442,145 column 2 line 63 to column 3 line 31.

Free isocyanate groups are not stable, i.e., the isocyanate groups will react with water or compounds that contain

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reactive hydrogen atoms. In order to provide stable and storable isocyanates and/or isocyanate-containing compounds, the NCO groups may be blocked with certain selected organic compounds that render the isocyanate group inert to reactive hydrogen compounds at room temperature. When heated to elevated temperatures, e.g., between 90 and 200°C, the blocked isocyanates release the blocking agent and react in the same way as the original unblocked or free isocyanate.

In one non-limiting embodiment, the isocyanates can be fully blocked, as described in U.S. Patent 3,984,299, column 1, lines 1 to 68, column 2 and column 3, lines 1 to 15, or partially blocked and reacted with the polymer backbone, as described in U.S. Patent 3,947,338, column 2, line 65 to column 4, line 30. As used herein, the NCO in the NCO:OH ratio represents the free or reactive isocyanate of the free isocyanate-containing compounds and blocked or partially blocked isocyanate-containing compounds after the release of the blocking agent. In some cases, it is not possible to remove all of the blocking agent. In those situations, more of the blocked isocyanate-containing compound would be used to attain the desired level of free NCO.

In another non-limiting embodiment, the isocyanate-containing compound is chosen from the modified or unmodified group of compounds of aliphatic isocyanates, cycloaliphatic isocyanates, aromatic isocyanates, partially blocked aliphatic isocyanates, partially blocked cycloaliphatic isocyanates, partially blocked aromatic isocyanates or a mixture thereof. In another non-limiting embodiment, the isocyanate is chosen from the modified group of aliphatic isocyanates, cycloaliphatic isocyanates, aromatic isocyanates or a mixtures thereof. In a further non-limiting embodiment, the isocyanate component is an unmodified aliphatic isocyanate.

Generally, compounds used to block the isocyanates are certain organic compounds that have active hydrogen atoms. In one non-limiting embodiment, examples include volatile alcohols, amines, acidic esters, epsilon-caprolactam, triazoles, pyrazoles and ketoxime compounds. In another non-limiting embodiment, the blocking compounds can be selected from the group consisting of methanol, t-butanol, phenol, cresol, nonylphenol, diisopropyl

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amine, malonic acid diethyl ester, acetoacetic acid ethyl ester, epsilon-caprolactam, 3-aminotriazole, 1,2,4-triazole, pyrazole, 3,5-dimethyl pyrazole, acetone oxime, methyl amyl ketoxime, methyl ethyl ketoxime or a mixture thereof. In a further non-limiting  
5 embodiment, the blocking compound is chosen from methanol, diisopropyl amine, malonic acid diethyl ester, acetoacetic acid ethyl ester, 1,2,4-triazole, methyl ethyl ketoxime, acetone oxime or a mixture thereof. In a still further non-limiting embodiment, the blocking compound is methanol, diisopropyl amine, methyl ethyl  
10 ketoxime, 1,2,4-triazole or a mixture thereof.

In one non-limiting embodiment, the NCO:OH ratio for the monoisocyanate containing material having at least one unsaturated group to the material comprising at least one carbonate group and at least one hydroxyl can range from 1:1 to  
15 1:7, e.g., from 1:2 to 1:6 or from 1:2 to 1:5. The NCO:OH ratio can range between any combination of these values, inclusive of the recited ranges, e.g., from 1:1.5 to 1:6.9.

In another non-limiting embodiment, the molecular weight of the reaction product of at least one material comprising  
20 at least one carbonate group and at least one hydroxyl group and at least one monoisocyanate containing material having at least one unsaturated group, e.g., component (a), can vary widely. It can range from the molecular weight of the minimal number of elements used to form the reaction product, about 200 grams per  
25 mole, to a large polymeric species having a number average molecular weight based on polystyrene standards of 200,000. For example, the molecular weight can range from a number average molecular weight range based on polyethylene glycol standards of from 500 to 17,500 or a number average molecular weight range  
30 based on polystyrene standards from 1500 to 100,000. The molecular weight of the reaction product can range between any combination of these values, e.g., from a molecular weight of 250 grams per mole to a number average molecular weight of 150,000. In one contemplated non-limiting embodiment, the molecular weight of  
35 component (a) is a number average molecular weight based on polystyrene standards of greater than 2,000.

In a series of non-limiting embodiments, component (a) can be present in the photochromic polymerizable composition in a

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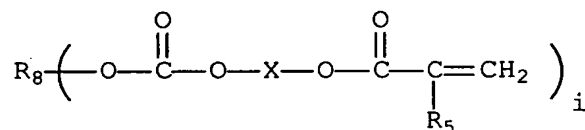
wide range of amounts, e.g., from 5 to 100 percent by weight based on the total weight of the polymerizable non-photochromic components. Component (a) can be present in the polymerizable composition of the present invention in an amount of at least 5 percent by weight, e.g., in an amount of at least 20 percent by weight, or least 30 percent by weight, the percent weights being based on the total weight of the polymerizable non-photochromic components. Component (a) can be present in the polymerizable composition in an amount of less than 95 percent by weight, e.g., in an amount of less than 75 percent by weight, or less than 50 percent by weight, the percent weights being based on the total weight of the polymerizable non-photochromic components. The amount of component (a) monomer that is present in the polymerizable composition of the present invention can range between any combination of these upper and lower values, inclusive of the recited values, e.g. from 6 to 99 weight percent.

In another series of non-limiting embodiments, the copolymerizable monomer of optional component (b) can be present in the photochromic polymerizable composition in a wide range of amounts. The copolymerizable monomer(s) can be present in the polymerizable composition in an amount of at least 5 percent by weight, e.g., in an amount of at least 25 percent by weight, or at least 50 percent by weight, the percent weights being based on the total weight of the polymerizable non-photochromic components. The copolymerizable monomer(s) can be present in the polymerizable composition in an amount of less than 95 percent by weight, e.g., in an amount less than 80 percent by weight, or less than 70 percent by weight, the percent weights being based on the total weight of the polymerizable non-photochromic components. The amount of copolymerizable monomer that is present in the polymerizable composition can range between any combination of these upper and lower values, inclusive of the recited values, e.g., from 10 to 90 weight percent. The weight percent of component (a) and component (b), based on the total weight of the polymerizable non-photochromic components, comprises 100 weight percent.

In one non-limiting embodiment, the first copolymerizable monomer of the polymerizable organic composition

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of the present invention can be described as (meth)acryloyl terminated carbonates of linear or branched aliphatic polyols, cycloaliphatic polyols, aromatic polyols or polyols comprising ester groups, e.g., aliphatic glycol bis((meth)acryloyl carbonate) monomers, alkylidene bisphenol bis((meth)acryloyl carbonate) monomers or polyester bis((meth)acryloyl carbonate) monomers. Non-limiting methods for preparation of the first monomer are procedures described in U.S. Patent 5,965,680.



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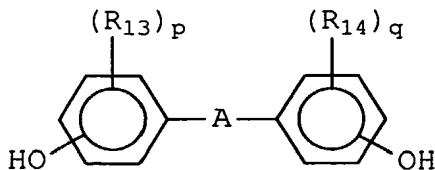
With reference to the above formula,  $R_8$  is a polyvalent residue of a polyol, which can be an aliphatic polyol, cycloaliphatic polyol, an aromatic polyol or a polyol comprising ester groups containing at least 2 hydroxy groups, e.g., 3, 4, 5 or 6 hydroxy groups. Polyols having more than 2 hydroxy groups include, for example, glycerol, trimethylol propane, trimethylol ethane, di-trimethylol propane, di-trimethylol ethane, pentaerythritol and di-pentaerythritol. X is a divalent linking group defined hereinbefore,  $R_5$  is hydrogen or methyl. In one non-limiting embodiment  $R_5$  is methyl, the letter  $i$  is an integer from 2 to 6. In another non-limiting embodiment,  $i$  is 2.

In a series of non-limiting embodiments, the polyol of which  $R_8$  is a residue contains 2 hydroxy groups, i.e., a diol, such as a glycol or bisphenol. The aliphatic polyol can be linear or branched and contain from 2 to 20 carbon atoms. In one non-limiting embodiment, the aliphatic polyol is an alkylene glycol having from 2 to 4 carbons atoms, e.g., ethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, and/or a poly( $C_2$ - $C_4$ ) alkylene glycol, e.g., diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, etc.

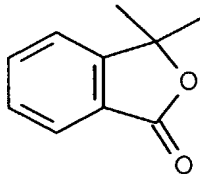
In a further non-limiting embodiment, the polyol of which  $R_8$  is a residue can also be chosen from 1,3-benzene diol,

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1,4-benzene diol, hydroxyquinone bis(2-hydroxyethyl)ether or a bisphenol represented by the following formula,



5 wherein  $R_{13}$  and  $R_{14}$  are each independently chosen for each occurrence from  $C_1$ - $C_4$  alkyl, chlorine or bromine;  $p$  and  $q$  are each independently chosen from an integer from 0 to 4; and  $-A-$  is a divalent linking group chosen from  $-O-$ ,  $-S-$ ,  $-S(O_2)-$ ,  $-C(O)-$ ,  $-CH_2-$ ,  $-CH=CH-$ ,



10  $-C(CH_3)_2-$ ,  $-C(CH_3)(C_6H_5)-$  or

In a still further non-limiting embodiment, cycloaliphatic polyols from which  $R_8$  can be chosen include: 1,2-, 1,3- or 1,4-dimethanol cyclohexane, or hydrogenated versions of bisphenols, e.g., biscyclohexanols as described further herein. A  
15 non-limiting example of a biscyclohexanol from which  $R_8$  can be selected is 4,4'-isopropylidenebis(cyclo-hexanol).

In another non-limiting embodiment of the present invention, the polyol of which  $R_8$  is a residue is chosen from alkylene glycol, poly( $C_2$ - $C_4$ ) alkylene glycol, glycerol, 1,3-  
20 benzene diol, 1,4-benzene diol, hydroxyquinone bis(2-hydroxyethyl)ether diols, or a mixture thereof. In a further non-limiting embodiment, the polyol of which  $R_8$  is a residue is chosen from alkylene glycol, e.g., ethylene glycol, or poly( $C_2$ - $C_4$ ) alkylene glycol, e.g., diethylene glycol.

25 Examples of polyol((meth)acryloyl carbonate) monomers from which the first copolymerizable monomer (a) can be chosen include, but are not limited to: ethylene glycol bis((methacryloyloxy)ethylene carbonate), ethylene glycol bis((acryloyloxy)ethylene carbonate), diethylene glycol  
30 bis((methacryloyloxy)ethylene carbonate), diethylene glycol

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bis((acryloyloxy)ethylene carbonate), triethylene glycol  
 bis((methacryloyloxy)ethylene carbonate), triethylene glycol  
 bis((acryloyloxy)ethylene carbonate), propylene glycol  
 bis((methacryloyloxy)ethylene carbonate), propylene glycol  
 5 bis((acryloyloxy)ethylene carbonate), 1,3-propanediol  
 bis((methacryloyloxy)ethylene carbonate), 1,3-propanediol  
 bis((acryloyloxy)ethylene carbonate), 1,3-butanediol  
 bis((methacryloyloxy)ethylene carbonate), 1,3-butanediol  
 bis((acryloyloxy)ethylene carbonate), 1,2- and 1,3-glycerol  
 10 bis((methacryloyloxy)ethylene carbonate), 1,2- and 1,3-glycerol  
 bis((acryloyloxy)ethylene carbonate), 1,4 butanediol  
 bis((methacryloyloxy)ethylene carbonate), 1,4 butanediol  
 bis((acryloyloxy)ethylene carbonate), dipropylene glycol  
 bis((methacryloyloxy)ethylene carbonate), dipropylene glycol  
 15 bis((acryloyloxy)ethylene carbonate), trimethyleneglycol  
 bis((methacryloyloxy)ethylene carbonate), trimethyleneglycol  
 bis((acryloyloxy)ethylene carbonate), pentamethylene glycol  
 bis((methacryloyloxy)ethylene carbonate), pentamethylene glycol  
 bis((acryloyloxy)ethylene carbonate), 1,3- and 1,4-benzene diol  
 20 bis((methacryloyloxy)ethylene carbonate), 1,3- and 1,4-benzene  
 diol bis((acryloyloxy)ethylene carbonate), hydroxyquinone bis(2-  
 hydroxyethyl)ether bis((methacryloyloxy)ethylene carbonate),  
 hydroxyquinone bis(2-hydroxyethyl)ether bis((acryloyloxy)ethylene  
 carbonate), isopropylidene bisphenol bis((methacryloyloxy)ethylene  
 25 carbonate), isopropylidene bisphenol bis((acryloyloxy)ethylene  
 carbonate), diethyleneglycol bis((methacryloyloxy)2-methyl-  
 ethylene carbonate), diethyleneglycol bis((methacryloyloxy)1,4-  
 cyclohexylene carbonate), diethyleneglycol  
 bis((methacryloyloxy)1,4-phenylene carbonate), diethyleneglycol  
 30 bis((methacryloyloxy)2,5-dimethyl-1,3-phenylene carbonate) or a  
 mixture thereof.

In a further non-limiting embodiment, the polyol of  
 which  $R_8$  is a residue of is a polyol comprising ester groups.  
 Such polyols are generally known and can have a number average  
 35 molecular weight in the range of from 200 to 10,000. They can be  
 prepared by conventional techniques utilizing low molecular weight  
 diols, i.e., diols having a molecular weight of 500 grams per mole  
 or less, triols and polyhydric alcohols known in the art,

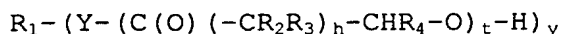
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(optionally in combination with monohydric alcohols) with polycarboxylic acids. Non-limiting examples of polycarboxylic acids include: phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, adipic acid, succinic acid, glutaric acid, fumaric acid, or mixtures thereof.

Anhydrides of the above acids, where they exist, can also be employed and are encompassed by the term "polycarboxylic acid".

In a still further non-limiting embodiment, certain materials which react in a manner similar to acids to form polyester polyols are also useful. Such materials include lactones, e.g., caprolactone, propiolactone and butyrolactone, and hydroxy acids such as hydroxycaproic acid and dimethylol propionic acid. If a triol or polyhydric alcohol is used, a monocarboxylic acid, such as acetic acid and/or benzoic acid, can be used in the preparation of the polyester polyols, and for some purposes, such a polyester polyol can be desirable. Moreover, polyester polyols are understood herein to include polyester polyols modified with fatty acids or glyceride oils of fatty acids (i.e., conventional alkyd polyols containing such modification). Other non-limiting examples of polyester polyols which can be utilized are those prepared by reacting an alkylene oxide, e.g., ethylene oxide, propylene oxide, etc., and the glycidyl esters of versatic acid with methacrylic acid to form the corresponding ester.

In one non-limiting embodiment, when  $R_8$  is the residue of a polyol comprising ester groups, the polyol from which it is a residue can be represented by the following formula:



wherein: Y is -O- or -NR- and R is hydrogen or  $C_1$ - $C_{12}$  alkyl;  $R_1$  is an organic radical derived from an initiator. Initiators are compounds having at least one reactive hydrogen capable, with or without the aid of a catalyst, of opening the lactone ring and adding it as an open chain without forming water of condensation. Non-limiting examples of initiators include monofunctional initiators such as alcohols and amines, and polyfunctional initiators such as polyols, polyamines, aminoalcohols, and vinyl polymers, as well as amides, sulfonamides, hydrozones, semicarbazones, oximes, polycarboxylic acids, hydroxy carboxylic

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acids and amino-carboxylic acids.  $R_2$ ,  $R_3$  and  $R_4$  are each chosen independently for each occurrence from hydrogen,  $C_1$ - $C_{12}$  alkyl,  $C_5$ - $C_6$  cycloalkyl,  $C_1$ - $C_6$  alkoxy, benzyl or phenyl, provided that at least  $h+2$  of the total number of  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen. For  
5 example, when butyrolactone ( $C_4H_6O_2$ ) is the starting material,  $h$  is 2 and at least 4, actually 5 of the total number of  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen. The letter  $h$  is chosen from an integer from 1 to 6;  $t$  is chosen from an integer from 1 to 100; and  $y$  is chosen from an integer equal to from 2 to 6.

10 In another non-limiting embodiment, the polyol comprising ester groups is the reaction product of a diol initiator and a lactone, i.e., a polylactone diol. The diol of the polylactone diol can be chosen from linear or branched aliphatic diols having from 2 to 20 carbon atoms, poly( $C_2$ -  
15  $C_4$ )alkylene glycols, cycloaliphatic diols having from 5 to 8 carbon atoms in the cyclic ring, monocyclic aromatic diols, bisphenols, hydrogenated bisphenols or a mixture thereof.

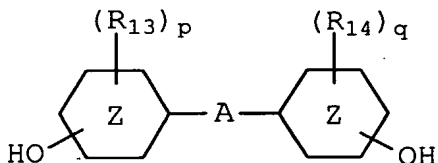
Examples of linear or branched aliphatic diols having from 2 to 20 carbon atoms that can be used to prepare the  
20 polylactone diol include, but are not limited to, the diols of which  $R_8$  is a residue. Non-limiting examples of such diols include: ethylene glycol, propylene glycol, 1,3-propane diol, 1,2- and 2,3-butane diol, pentane diols, hexane diols, heptane diols, octane diols, nonane diols, decane diols, undecane diols, dodecane  
25 diols, tridecane diols, tetradecane diols, pentadecane diols, hexadecane diols, heptadecane diols, octadecane diols, nonadecane diols and icosane diols. Examples of poly( $C_2$ - $C_4$ )alkylene glycols include, but are not limited to, di-, tri-, tetra-, penta- and higher ethylene glycols, di-, tri-, tetra-, penta- and higher  
30 propylene glycols, and di-, tri-, tetra-, penta- and higher butylene glycols.

Cycloaliphatic diols having from 5 to 8 carbon atoms that can be used to prepare the polylactone diol include, but are not limited to, those cycloaliphatic diols described previously  
35 herein, cyclopentane diol, cyclohexane diol, cyclohexane dimethanol, cycloheptane diol and cyclooctane diol. Examples of monocyclic aromatic diols that can be used to prepare the polylactone diol include but are not limited to, benzene diol,

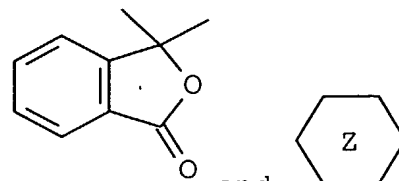
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e.g., 1,2-dihydroxy benzene and 1,3-dihydroxy benzene; C<sub>1</sub>-C<sub>4</sub> alkyl substituted benzene diol, e.g., 4-tert-butyl-benzene-1,2-diol, 4-methyl-benzene-1,2-diol, 3-tert-butyl-5-methyl-benzene-1,2-diol and 3,4,5,6-tetramethyl-benzene-1,2-diol; halo substituted benzene diol, e.g., 3,5-dichlorobenzene-1,2-diol, 3,4,5,6-tetrabromo-benzene-1,2-diol and 3,4,5-trichloro-benzene-1,2-diol; and C<sub>1</sub>-C<sub>4</sub> alkyl and halo substituted benzene diol, e.g., 3-bromo-5-tert-butyl-benzene-1,2-diol, 3,6-dichloro-4-methyl-benzene-1,2-diol, 3-bromo-4,5-dimethyl-benzene-1,2-diol or 3-chloro-4,6-di-tert-butyl-benzene-1,2-diol.

In one non-limiting embodiment, bisphenols and hydrogenated bisphenols that can be used to prepare the polylactone diol can be represented by the following formula:



wherein R<sub>13</sub> and R<sub>14</sub> are each independently chosen for each occurrence from C<sub>1</sub>-C<sub>4</sub> alkyl, chlorine or bromine; p and q are each independently chosen from an integer from 0 to 4; and -A- is a divalent linking group chosen from -O-, -S-, -S(O<sub>2</sub>)-, -C(O)-, -

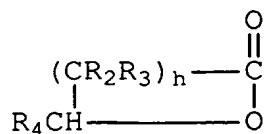


CH<sub>2</sub>-, -CH=CH-, -C(CH<sub>3</sub>)<sub>2</sub>-, -C(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)- or

represents a benzene ring or a cyclohexane ring. A non-limiting example of a bisphenol that can be used to prepare the polylactone diol is 4,4'-isopropylidenebisphenol. A non-limiting example of a hydrogenated bisphenol that can be used to prepare the polylactone diol is 4,4'-isopropylidenebiscyclohexanol.

In one non-limiting embodiment, the lactone used to prepare the polylactone diol has from 3 to 8 carbon atoms in the cyclic lactone ring and can be represented by the following formula,

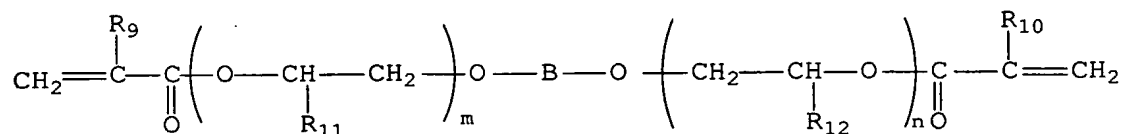
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wherein h is chosen from an integer from 1 to 6, e.g., 1, 2, 3, 4, 5 or 6, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each chosen independently for each occurrence from hydrogen, C<sub>1</sub>-C<sub>12</sub> alkyl, C<sub>5</sub>-C<sub>6</sub> cycloalkyl, C<sub>1</sub>-C<sub>6</sub> alkoxy, benzyl or phenyl, provided that at least h+2 of the total number of R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> groups are hydrogen. In another non-limiting embodiment, each of R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each hydrogen.

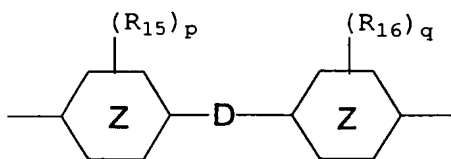
Examples of lactones that can be used to prepare the poly(lactone diol include, but are not limited to: beta-propiolactone; gamma-butyrolactone; beta-butyrolactone; delta-valerolactone; alpha-methyl-gamma-butyrolactone; beta-methyl-gamma-butyrolactone; gamma-valerolactone; epsilon-caprolactone; monomethyl-, monoethyl-, monopropyl-, monoisopropyl- etc. through monododecyl epsilon-caprolactones; methoxy and ethoxy epsilon-caprolactones; cyclohexyl epsilon-caprolactones; phenyl epsilon-caprolactones; benzyl epsilon-caprolactones; zeta-enantholactone; and eta-capryllactone. In one non-limiting embodiment of the present invention, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each hydrogen, h is 4 and the lactone is epsilon-caprolactone.

In one non-limiting embodiment, the second copolymerizable monomer can be represented by the following formula:

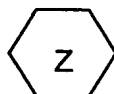


wherein m and n are each independently chosen from an integer from 0 to 6, the sum of m and n being from 0 to 6, R<sub>9</sub> and R<sub>10</sub> are each independently chosen from hydrogen or methyl, R<sub>11</sub> and R<sub>12</sub> are each independently chosen for each occurrence from hydrogen or C<sub>1</sub> to C<sub>2</sub> alkyl, and B is a divalent linking group chosen from straight or branched chain alkylene, phenylene, C<sub>1</sub>-C<sub>4</sub> alkyl substituted phenylene, or a group represented by the following formula,

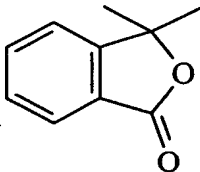
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wherein  $R_{15}$  and  $R_{16}$  are each independently chosen for each occurrence from  $C_1$ - $C_4$  alkyl, chlorine or bromine,  $p$  and  $q$  are each



chosen from an integer from 0 to 4, represents a divalent 5 benzene group or a divalent cyclohexane group and  $D$  is  $-O-$ ,  $-S-$ ,  $-S(O_2)-$ ,  $-C(O)-$ ,  $-CH_2-$ ,  $-CH=CH-$ ,  $-C(CH_3)_2-$ ,



$-C(CH_3)(C_6H_5)-$  or



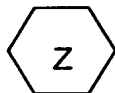
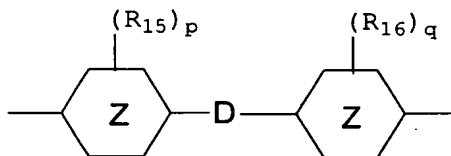
when

is the divalent



benzene group, and  $D$  is  $-O-$ ,  $-S-$ ,  $-CH_2-$ , or  $-C(CH_3)_2-$  when is the divalent cyclohexane group.

10 In one non-limiting embodiment,  $B$  is a divalent linking group represented by the following formula,

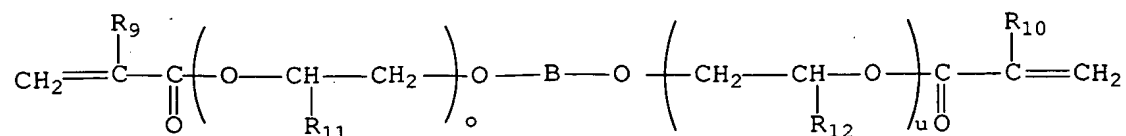


wherein represents a benzene group.

In another non-limiting embodiment,  $R_9$  and  $R_{10}$  are each 15 methyl,  $R_{11}$ , and  $R_{12}$  are each hydrogen,  $p$ ,  $q$ ,  $r$  and  $s$  are each 0,  $D$  is  $-C(CH_3)_2-$  and the sum of  $m$  and  $n$  is chosen from 0 to 4.

In one non-limiting embodiment, the third copolymerizable monomer can be represented by the following formula:

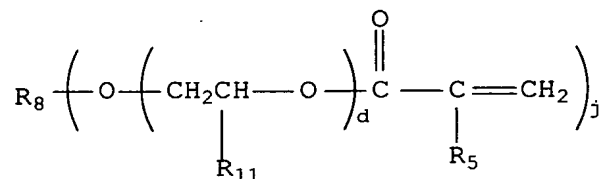
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wherein o and u are each independently chosen from a positive number, the sum of o and u being chosen from 7 to 70, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub> and B are the same as defined hereinbefore.

In another non-limiting embodiment, the sum of o and u is from 10 to 30.

In one non-limiting embodiment, the fourth copolymerizable monomer can be represented by the following formula:



wherein R<sub>5</sub>, R<sub>8</sub> and R<sub>11</sub> are the same as defined hereinbefore, d is chosen from a number from 0 to 20, and j is chosen from a number from 3 to 6.

In another non-limiting embodiment, d is from 3 to 15 and the polyol from which R<sub>8</sub> is derived is trimethylolpropane, pentaerythritol or dipentaerythritol. In a further non-limiting embodiment, d is from 5 to 10.

In one non-limiting embodiment, the fifth copolymerizable monomer can be the reaction product of a polycarbonate polyol polychloroformate and a hydroxy(meth)acrylate. It can be prepared by a method comprising:

(a) preparing a chloroformate intermediate of the polyol comprising carbonate group(s); and

(b) reacting the chloroformate groups of the chloroformate intermediate with a hydroxy(meth)acrylate.

Preparation of the chloroformate intermediates and the subsequent reaction with hydroxy functional (meth)acrylate can be conducted in accordance with art-recognized methods. As is known to the skilled artisan, the reaction of chloroformate groups with

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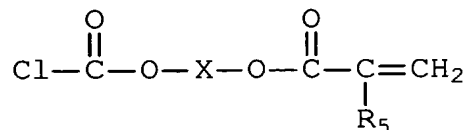
a hydroxy functional (meth)acrylate is typically performed in the presence of an acid scavenger, e.g., an alkali metal hydroxide, followed by washing and isolation of the resulting mixture of polyol((meth)acryloyl carbonate) monomers. While the molar

5 equivalents ratio of hydroxy functional (meth)acrylate to chloroformate groups of the mixture of chloroformate intermediates in step (b) can be less than 1:1, in one non-limiting embodiment it is at least 1:1 (i.e., all of the chloroformate groups are reacted with hydroxy (meth)acrylate). In step (b) of the method,

10 the molar equivalents ratio of hydroxy (meth)acrylate to chloroformate groups can be from 1:1 to 1.5:1.0, e.g., 1.1:1.0.

In another non-limiting embodiment, the fifth copolymerizable monomer can also be prepared by a method comprising reacting the hydroxy groups of the polyol comprising

15 carbonate groups with a chloroformate functional (meth)acrylate represented by the following formula:



wherein X and R<sub>5</sub> are each as described previously herein.

20 The chloroformate functional (meth)acrylate represented by the aforementioned formula can be prepared by methods that are well known to the skilled artisan. In one non-limiting embodiment, a hydroxy functional (meth)acrylate, such as 2-hydroxyethyl(meth)acrylate, is reacted with phosgene in a molar

25 equivalents ratio such that the chloroformate functional (meth)acrylate represented by the aforementioned formula is formed.

In one non-limiting embodiment, the reaction of the hydroxy groups of the polyol(s) with the chloroformate groups of

30 the chloroformate functional (meth)acrylate is performed in the presence of an acid scavenger, e.g., an alkali metal hydroxide, followed by washing and isolation of the resulting mixture of polyol((meth)acryloyl carbonate) monomers (as is known to the skilled artisan). While the molar equivalents ratio of hydroxy

35 groups of the mixture of polyols to chloroformate groups of the

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chloroformate functional (meth)acrylate can vary widely, in one non-limiting embodiment, it is chosen such that all of the hydroxy groups of the mixture of polyols are reacted with chloroformate functional (meth)acrylate, i.e., a molar equivalents ratio of less than or equal to 1:1, e.g., from 0.5:1 to 1:1.

In another non-limiting embodiment, the fifth copolymerizable monomer can be prepared by reacting a polyol (in excess) with (meth)acryloyl chloride followed by washing and isolation of the monofunctional methacrylate. This material is reacted with phosgene to form a chloroformate intermediate that is subsequently reacted with a polyol comprising at least one carbonate group.

In one non-limiting embodiment, the sixth copolymerizable monomer can be prepared by reacting a polycarbonate polyol with (meth)acryloyl chloride (in excess) followed by washing and isolation of polycarbonate polyol(meth)acrylate.

In one non-limiting embodiment, the seventh copolymerizable monomer is a monoethylenically unsaturated monomer that is polymerizable by free radical initiation. The monoethylenically unsaturated monomer can be chosen from an alkyl ester of (meth)acrylic acid, vinyl aromatic monomer, vinyl halide, vinylidene halide, vinyl ester, (meth)acryloxypropyltri(C<sub>1</sub>-C<sub>4</sub>)alkoxysilane, (meth)acrylic acid or a mixture thereof.

In another non-limiting embodiment, the monoethylenically unsaturated monomer can be chosen from stearyl methacrylate, methyl methacrylate, isobornyl methacrylate, phenoxyethyl methacrylate, cyclohexyl methacrylate, styrene, vinyl toluene, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene fluoride, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl pyrrolidinone, vinyl benzoate, methacryloxypropyltrimethoxysilane or a mixture thereof.

In one non-limiting embodiment, the eighth copolymerizable monomer is an allyl functional monomer having at least two allyl groups. The allyl functional monomer can be used in the polymerizable composition at a level that does not exceed 5 weight percent, based on the total weight of the monomers. In

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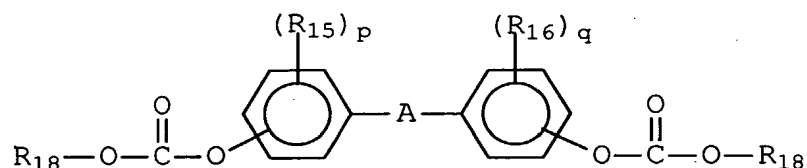
another non-limiting embodiment, the allyl functional monomer is chosen from:

(i) an allyl functional monomer represented by the following formula,

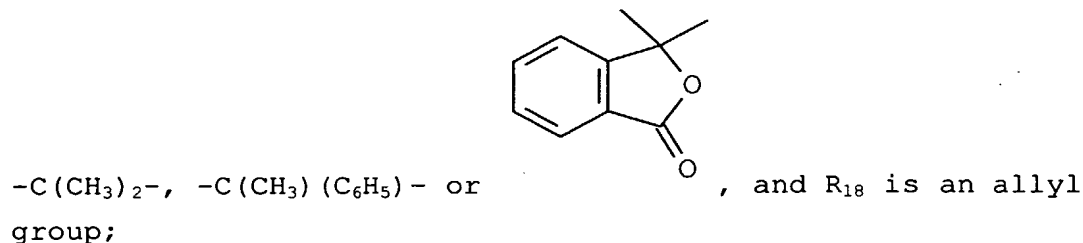


wherein  $R_{17}$  is a divalent residue of a diol chosen from 1,2-ethane diol diethylene glycol or 1,2-propane diol, and  $R_{18}$  is an allyl group;

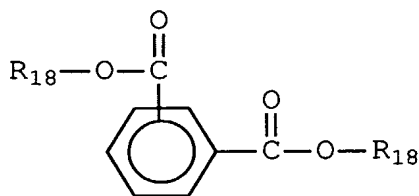
(ii) an allyl functional monomer represented by the following formula:



wherein  $R_{15}$  and  $R_{16}$  are each independently chosen for each occurrence from each other from  $C_1$ - $C_4$  alkyl, chlorine or bromine,  $p$  and  $q$  are each independently chosen from an integer from 0 to 4, and  $-A-$  is a divalent linking group chosen from  $-O-$ ,  $-S-$ ,  $-S(O_2)-$ ,  $-C(O)-$ ,  $-CH_2-$ ,  $-CH=CH-$ ,



(iii) an allyl functional monomer represented by the following formula:



wherein  $R_{18}$  is an allyl group; or

(iv) a mixture of at least two of (i), (ii) and (iii).

In a further non-limiting embodiment, the allyl functional monomer is chosen from:

(i) polyether diol bis(allyl carbonate);

(ii) polylactone diol bis(allyl carbonate); or

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(iii) a mixture thereof.

In one non-limiting embodiment, polymerization of the photochromic polymerizable coating composition can occur by mechanisms described in the definition of "polymerization" in  
5 Hawley's Condensed Chemical Dictionary Thirteenth Edition, 1997, John Wiley & Sons, pages 901-902. Those mechanisms include by "addition", in which free radicals are the initiating agents that react with the double bond of the monomer by adding to it on one side at the same time producing a new free electron on the other  
10 side, by "condensation", involving the splitting out of water molecules by two reacting monomers and by so-called "oxidative coupling"

In a further non-limiting embodiment, polymerization of the photochromic polymerizable coating composition can be  
15 accomplished by adding to the composition an initiating amount of material capable of generating free radicals, such as organic peroxy compounds or azobis(organonitrile) compounds, i.e., an initiator. Methods for polymerizing polyol((meth)acryloyl carbonate) monomer compositions are well known to the skilled  
20 artisan and any of those well known techniques can be used to polymerize the aforescribed polymerizable organic compositions. Such polymerization methods include thermal polymerization, photopolymerization or a combination thereof.

Non-limiting examples of organic peroxy compounds, that  
25 can be used as thermal polymerization initiators include: peroxy monocarbonate esters, such as tertiarybutylperoxy isopropyl carbonate; peroxydicarbonate esters, such as di(2-ethylhexyl) peroxydicarbonate, di(secondary butyl) peroxydicarbonate and diisopropylperoxydicarbonate; diacyperoxides, such as 2,4-  
30 dichlorobenzoyl peroxide, isobutyryl peroxide, decanoyl peroxide, lauroyl peroxide, propionyl peroxide, acetyl peroxide, benzoyl peroxide and p-chlorobenzoyl peroxide; peroxyesters such as t-butylperoxy pivalate, t-butylperoxy octylate and t-butylperoxyisobutyrate; methylethylketone peroxide, and  
35 acetylcyclohexane sulfonyl peroxide. In one non-limiting embodiment the thermal initiators used are those that do not discolor the resulting polymerizate.

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Non-limiting examples of azobis(organonitrile) compounds, that can be used as thermal polymerization initiators include: azobis(isobutyronitrile), azobis(2,4-dimethylvaleronitrile) or a mixture thereof.

5           The amount of thermal polymerization initiator used to initiate and polymerize the photochromic polymerizable coating composition can vary and will depend on the particular initiator used and the intended photochromic article, e.g., coated lens or overmold. Only that amount that is required to initiate and  
10 sustain the polymerization reaction is required, i.e., an initiating amount. With respect to the peroxy compound, diisopropyl peroxydicarbonate, used in one non-limiting embodiment, the amount is typically between 0.01 and 3.0 parts of that initiator per 100 parts of the polymerizable organic  
15 composition (phm). In another non-limiting embodiment, between 0.05 and 1.0 phm is used to initiate the polymerization. The thermal cure cycle involves heating the photochromic polymerizable coating composition in the presence of the initiator, in one non-limiting embodiment, from room temperature to 85°C to 125°C over a  
20 period of from 2 hours to 30 hours.

In one non-limiting embodiment, photopolymerization of the photochromic polymerizable coating composition according to the present invention can be carried out in the presence of a photopolymerization initiator using ultraviolet light, visible  
25 light, or a combination thereof. Non-limiting examples of photopolymerization initiators include benzoin, benzoin methyl ether, benzoin isobutyl ether benzophenol, acetophenone, 4,4'-dichlorobenzophenone, diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-hydroxycyclohexyl phenyl ketone, 2-  
30 isopropylthioxantone and 2,4,6-trimethylbenzoyldiphenylphosphine oxide. The amount of photopolymerization initiator used to initiate and polymerize the polymerizable organic compositions of the present invention can vary and will depend on the particular initiator used and the intended photochromic article to be  
35 produced. Only that amount that is required to initiate and sustain the polymerization reaction is required, i.e., an initiating amount. In one non-limiting embodiment, the photopolymerization initiator is used in an amount from 0.01

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percent to 5 percent by weight, based on the weight of monomer components.

In one non-limiting embodiment, the light source used for the photopolymerization is chosen from those which emit  
5 ultraviolet light. The light source can be a mercury lamp, a germicidal lamp or a xenon lamp. Visible light, e.g., sunlight, can also be used. The exposure time may differ depending upon, e.g., the wavelength and intensity of the light source and the particular photochromic article, and is typically determined  
10 empirically.

Non-limiting examples of photochromic compounds that can be utilized with the polymerizable coating compositions of the present invention are organic photochromic compounds that color to a desired hue. They typically have at least one activated  
15 absorption maxima within the range of between about 400 and 700 nanometers. They can be used individually or may be used in combination with photochromic compounds that complement their activated color.

In one non-limiting embodiment, the organic  
20 photochromic materials include chromenes, e.g., naphthopyrans, benzopyrans, indenonaphthopyrans and phenanthorpyrans; spiropyrans, e.g., spiro(benzindoline)naphthopyrans, spiro(indoline)benzopyrans, spiro(indoline)naphthopyrans, spiro(indoline)quinopyrans and spiro(indoline)pyrans; oxazines,  
25 e.g., spiro(indoline)naphthoxazines, spiro(indoline)pyridobenzoxazines, spiro(benzindoline)pyridobenzoxazines, spiro(benzindoline)naphthoxazines and spiro(indoline)benzoxazines; mercury dithizonates, fulgides, fulgimides and mixtures of such  
30 photochromic compounds. Such photochromic compounds are described in U.S. Patents 5,645,767 6,153,126 and 6,296,785B1 at column 30, line 44 to column 31, line 5.

In another non-limiting embodiment, the photochromic compounds described herein are used in photochromic amounts and in  
35 a ratio (when mixtures are used) such that a coating composition to which the compound(s) is applied or in which it is incorporated exhibits a desired resultant color, e.g., a substantially neutral color such as shades of gray or brown when activated with

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unfiltered sunlight, e.g., as near a neutral color as possible given the colors of the activated photochromic compounds. Neutral gray and neutral brown colors are preferred in one non-limiting embodiment; however, other fashionable colors can also be used.

5 Further discussion of neutral colors and ways to describe colors can be found in U.S. Patent 5,645,767 column 12, line 66 to column 13, line 19.

As used herein and in the claims, by "photochromic amount" is meant that amount of photochromic compound or substance  
10 which is at least sufficient to produce a photochromic effect discernible to the naked eye upon activation. The particular amount used depends often upon the intensity of color desired upon irradiation thereof. In one non-limiting embodiment, the more photochromic substance present in the polymerizable composition of  
15 the present invention or that which is incorporated into a coating of the present invention, the greater the color intensity of the resulting photochromic article.

The amount of photochromic material incorporated into the polymerizable coating composition, in one non-limiting  
20 embodiment, ranges from 0.01 to 40 weight percent based on the weight of the polymerizable composition. For example, the concentration of photochromic material can range from 0.05 to 30 weight percent, or from 0.1 to 20 weight percent or from 0.2 to 15 weight percent, e.g., from 7 to 14 weight percent, based on the  
25 weight of the polymerizable composition. The concentration of photochromic material can range between any combination of these values, inclusive of the recited ranges, e.g., from 0.05 to 39.95 weight percent.

When incorporated, e.g., by imbibition, into an at  
30 least partially cured coating of the present invention, the amount of photochromic substance applied to the surface can range, in one non-limiting embodiment, from 0.01 to 2.00, e.g., from 0.1 to 1.0, milligram per square centimeter of surface area. The concentration of photochromic material can range between any combination of  
35 these values, inclusive of the recited ranges, e.g., from 0.015 to 1.999 milligram per square centimeter of surface area. The term "imbibition" or "imbibe" is intended to mean and include permeation of the photochromic substance alone into the at least

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partially cured coating, solvent assisted transfer absorption of the photochromic substance into the at least partially cured coating, vapor phase transfer, and other such transfer mechanisms.

5 In various non-limiting embodiments, adjuvant materials can also be incorporated into the polymerizable coating composition with the photochromic material used, prior to, simultaneously with or subsequent to application or incorporation of the photochromic material in the polymerizable composition or  
10 cured coating. For example, ultraviolet light absorbers can be admixed with photochromic substances before their addition to the composition or such absorbers can be superposed, e.g., superimposed, as a layer between the photochromic coating and the incident light. Further, stabilizers can be admixed with the  
15 photochromic substances prior to their addition to the composition to improve the light fatigue resistance of the photochromic substances. Stabilizers, such as hindered amine light stabilizers (HALS), asymmetric diaryloxalamide (oxanilide) compounds and singlet oxygen quenchers, e.g., a nickel ion  
20 complex with an organic ligand, polyphenolic antioxidants or mixtures of such stabilizers are contemplated. They can be used alone or in combination. Such stabilizers are described in U.S. Patents 4,720,356, 5,391,327 and 5,770,115.

In one non-limiting embodiment, compatible (chemically  
25 and color-wise) tints, i.e., dyes, can be added to the polymerizable coating composition or applied to the coating to achieve a more aesthetic result, for medical reasons, or for reasons of fashion. The particular dye selected will vary and depend on the aforesaid need and result to be achieved. In one  
30 non-limiting embodiment, the dye can be selected to complement the color resulting from the activated photochromic substances, e.g., to achieve a more neutral color or absorb a particular wavelength of incident light. In another non-limiting embodiment, the dye can be selected to provide a desired hue to the coating when the  
35 photochromic substances are in an unactivated state.

In another non-limiting embodiment, various conventional additives can be incorporated into the photochromic polymerizable coating composition. Such additives can include

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heat stabilizers, mold release agents, static (non-photochromic) dyes, pigments, solvents and polymerization inhibitors to promote stability during storage. Antiyellowing additives, e.g., 3-methyl-2-butenol, organo pyrocarbonates and triphenyl phosphite  
5 [CAS 101-02-0], can also be added to polymerizable organic compositions of the present invention to enhance resistance to yellowing.

In a further non-limiting embodiment, the polymerizable coating composition of the present invention can  
10 further comprise additional conventional ingredients which impart desired characteristics to the composition, or which are required for the process used to apply and cure the composition to the substrate or which enhance the cured coating made therefrom. Such ingredients can be used in an amount up to 20 weight  
15 percent, based on the weight of the monomers. For example, plasticizers may be used to adjust the Fischer microhardness and/or photochromic performance properties of the photochromic polymerizable coating composition. Other such additional ingredients comprise rheology control agents, leveling agents,  
20 e.g., surfactants, free radical scavengers, cross linking agents and adhesion promoting agents.

Non-limiting examples of adhesion promoting agents such as organofunctional trialkoxysilanes having an alkoxy substituent of 1 to 4 carbon atoms and the polymerizable  
25 organofunctional silanes applied using the process disclosed in U.S. Patent 6,150,430 at column 2, line 39 to column 8; line 38 can be used. These materials include, but are not limited to:  $\gamma$ -glycidoxypropyltrimethoxysilane,  
 $\gamma$ -aminopropyltrimethoxysilane,  
30 methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, 3,4-epoxycyclohexylethyltrimethoxysilane, aminoethyltrimethoxysilane or a mixture thereof. Adhesion promoting agents can be used in an amount that improves the adhesion of a subsequently applied coating to the polymerizate of  
35 the present invention or an overmolding of the polymerizable composition to a lens blank. An adhesion improving amount of adhesion promoting agents is an amount that demonstrates an improved adhesion rating as measured by ASTM D-3359-Standard Test

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Method for Measuring Adhesion by Tape Test-Method B when compared to a coating without the adhesion promoter.

In one non-limiting embodiment, the substrates, i.e., materials to which the coating composition is applied, can be of any type such as, for example paper, glass, ceramics, wood, masonry, textiles, metals and organic polymeric materials. In one non-limiting embodiment, the substrate is an organic polymeric material, particularly, a solid transparent thermoset or thermoplastic organic polymeric materials, e.g., thermoplastic polycarbonate type polymers and copolymers, and homopolymers or copolymers of a polyol(allyl carbonate), used as organic optical materials.

The amount of the coating composition applied to the substrate in one non-limiting embodiment, is an amount necessary so that a sufficient quantity of the organic photochromic compound is incorporated, e.g., a photochromic amount, to produce a coating that exhibits a photochromic effect discernible to the naked eye when the cured coating is exposed to UV radiation. In another non-limiting embodiment, the cured coating can have a thickness of from 1 to 10,000 microns or from 5 to 1,000 microns or from 10 to 400 microns, e.g., 30 microns. The thickness of the applied coating can range between any combination of these values, inclusive of the recited values, e.g., from 1.1 to 9,999.9 microns.

In one non-limiting embodiment, the photochromic articles of the present invention having a coating of varying thickness can be produced by single or multiple coating applications using dip coating, spray coating, spin coating, spin and spray coating or a combination thereof. An alternate non-limiting method is the over molding process described hereinafter. It can be used alone or in combination with a coating method known in the art.

Following application of the coating composition to the treated surface of the substrate, in one non-limiting embodiment, the coating is cured. Methods for curing the photochromic polymerizable coating composition include the aforescribed methods. Additional non-limiting methods include irradiating the coating with infrared, gamma or electron radiation so as to

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initiate the polymerization reaction of the polymerizable components in the coating. This can be followed by a heating step.

If required and if appropriate, it is typical to clean the surface of the substrate to be coated prior to applying the coating composition of the present invention for the purposes of promoting adhesion of the coating. Effective treatment techniques for plastics and glass are known to those skilled in the art.

In some non-limiting embodiments, it may be necessary to apply a primer to the surface of the substrate before application of the coating composition of the present invention. The primer can serve as a barrier coating to prevent interaction of the coating ingredients with the substrate and vice versa, and/or as an adhesive layer to adhere the coating composition to the substrate. Application of the primer can be by any of the methods used in coating technology such as, for example, spray coating, spin coating, spin and spray coating, spread coating, dip coating, casting or roll-coating.

The use of protective coatings, some of which can contain polymer-forming organosilanes, as primers to improve adhesion of subsequently applied coatings has been described in U.S. 6,150,430. In one non-limiting embodiment, non-tintable coatings are used. Non-limiting examples of commercial coating products include SILVUE® 124 and HI-GARD® coatings, available from SDC Coatings, Inc. and PPG Industries, Inc., respectively. In addition, depending on the intended use of the coated article, in one non-limiting embodiment, it can be necessary to apply an appropriate protective coating(s), i.e., an abrasion resistant coating and/or coatings that serve as oxygen barriers, onto the exposed surface of the coating composition to prevent scratches from the effects of friction and abrasion and interactions of oxygen with the photochromic compounds, respectively. In some cases, the primer and protective coatings are interchangeable, e.g., the same coating can be used as the primer and the protective coating(s). Non-limiting examples of hardcoats include those based on inorganic materials such as silica, titania and/or zirconia as well as organic hardcoats of the type that are ultraviolet light curable.

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In one non-limiting embodiment, the article of the present invention comprises, in combination, a substrate, a photochromic polymerizable coating and a protective hardcoat. The protective hardcoat being an organosilane hardcoat.

5 In additional non-limiting embodiments, other coatings or surface treatments, e.g., a tintable coating, antireflective surface, etc., can also be applied to the articles of the present invention e.g., photochromic coated substrates. An antireflective coating, e.g., a monolayer or multilayer of metal oxides, metal  
10 fluorides, or other such materials, can be deposited onto the photochromic articles, e.g., lenses, of the present invention through vacuum evaporation, sputtering, or some other method.

In one non-limiting embodiment, the organic polymeric material that can be a substrate for the coating composition of  
15 the present invention will usually be transparent, but can be translucent or even opaque. Generally, the polymeric organic material is a solid transparent or optically clear material, e.g., materials suitable for optical applications, such as plano, ophthalmic and contact lenses, windows, automotive transparencies,  
20 e.g., windshields, aircraft transparencies, plastic sheeting, polymeric films, etc.

Non-limiting examples of polymeric organic materials which can be used as a substrate for the photochromic polymerizable coating composition described herein include:  
25 poly(meth)acrylates, polyurethanes, polythiourethanes, thermoplastic polycarbonates, polyesters, poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methyl methacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral, poly(vinyl acetate), cellulose  
30 acetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, polystyrene or polymers, such as homopolymers and copolymers of monomers chosen from bis(allyl carbonate) monomers, styrene monomers, diisopropenyl benzene monomers, vinylbenzene monomers, e.g., those described in U.S. Patent  
35 5,475,074, diallylidene pentaerythritol monomers, polyol (allyl carbonate) monomers, e.g., diethylene glycol bis(allyl carbonate), vinyl acetate monomers, acrylonitrile monomers, mono- or polyfunctional, e.g., di- or multi-functional, (meth)acrylate

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monomers such as (C<sub>1</sub>-C<sub>12</sub>)alkyl (meth)acrylates, e.g., methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate etc., poly(oxyalkylene) (meth)acrylate, poly(alkoxylated phenol (meth)acrylates), diethylene glycol (meth)acrylates, ethoxylated 5 bisphenol A (meth)acrylates, ethylene glycol (meth)acrylates, poly(ethylene glycol) (meth)acrylates, ethoxylated phenol (meth)acrylates, alkoxylated polyhydric alcohol (meth)acrylates, e.g., ethoxylated trimethylol propane triacrylate monomers, urethane (meth)acrylate monomers, such as those described in U.S. 10 Patent 5,373,033, or a mixture thereof. Further examples of polymeric organic host materials are disclosed in the U.S. Patent 5,753,146, column 8, line 62 to column 10, line 34.

In another non-limiting embodiment, transparent copolymers and blends of transparent polymers are also suitable as 15 polymeric materials. Typically, the substrate for the photochromic coating composition is an optically clear polymerized organic material prepared from a thermoplastic polycarbonate resin, such as the carbonate-linked resin derived from bisphenol A and phosgene, which is sold under the trademark, LEXAN; a 20 polyester, such as the material sold under the trademark, MYLAR; a poly(methyl methacrylate), such as the material sold under the trademark, PLEXIGLAS; polymerizates of a polyol(allyl carbonate) monomer, especially diethylene glycol bis(allyl carbonate), which monomer is sold under the trademark CR-39, and polymerizates of 25 copolymers of a polyol (allyl carbonate), e.g., diethylene glycol bis(allyl carbonate), with other copolymerizable monomeric materials, and copolymers with a polyurethane having terminal diacrylate functionality, as described in U.S. Patents 4,360,653 and 4,994,208; and copolymers with aliphatic urethanes, the 30 terminal portion of which contain allyl or acrylyl functional groups, as described in U.S. Patent 5,200,483.

One contemplated non-limiting embodiment, is the use of optically clear polymerizates, i.e., materials suitable for optical applications, such as optical elements, e.g., plano and 35 vision correcting ophthalmic lenses and contact lenses, windows, clear polymeric films, automotive transparencies, e.g., windshields, aircraft transparencies, plastic sheeting, etc. Such optically clear polymerizates may have a refractive index that may

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range from 1.48 to 2.00, e.g., from 1.495 to 1.75, particularly from 1.50 to 1.66.

Another contemplated non-limiting embodiment, is the use of a combination of the photochromic polymerizable coating composition of the present invention with optical elements to produce photochromic optical articles. Such articles can be prepared by sequentially applying to the optical element a primer, the photochromic polymerizable composition of the present invention and appropriate protective coating(s), if necessary.

10 In a further non-limiting embodiment, a semi-finished single vision (SFSV) lens having an adherent coating of the photochromic polymerizable composition of the present invention can be prepared by an overmolding process. Typically, a predetermined volume of the photochromic polymerizable composition  
15 is dispensed into a volume defined by a spherical concave or minus glass mold, which approximately matches the front surface curve and the outer diameter of a SFSV lens. The glass mold is fitted with a circular polyvinyl chloride gasket that extends approximately 0.2 millimeters above the mold and has an inside  
20 diameter approximately 4 millimeters less than outside diameter of the glass mold. After the monomer is dispensed, the SFSV lens is carefully placed on the dispensed polymerizable composition which spreads to fill the defined volume. A circular glass plate having an outside diameter equal to or greater than that of the lens is  
25 placed onto the rear surface of the lens. A spring clamp is positioned so that one side of the clamp is on the front surface of the negative mold and other side of the clamp is on the back surface of the glass plate. The resulting assembly is sealed by taping the circumference of the plate-lens-gasket-mold using  
30 polyurethane tape. The assembly is preheated in an air oven from 30 to 95°C for a 60 minute interval and subsequently the temperature is increased from 95 to 125°C and decreased to 82°C over a 3 hour interval. The assembly is separated by inserting a wedge beneath the gasket between the lens and mold. The lens now  
35 has an adherent coating of from 150 to 180 microns.

The present invention is more particularly described in the following examples which are intended as illustration only,

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since numerous modifications and variations therein will be apparent to those skilled in the art.

Components 1, 2 and 3 along with the Photochromic Component and various methacrylate monomers were used to produce 5 Examples 1 through 14. Example 15 describes the preparation and testing of the photochromic lenses of the examples and the results of that testing done according to the Accelerated Weathering Photochromic Percent Photopic Fatigue Test.

10 Component 1

The reaction product of an isocyanate and a polycarbonate polyol was prepared from the ingredients as summarized in Table 1.

15 Table 1

<u>Ingredients</u>		<u>Weight (grams)</u>
<u>Charge 1</u>		
PC-1122 (a)		936.10
THF (b)		500.00
20 MEHQ (c)		0.20
<u>Charge 2</u>		
ICEMA (d)		155.16
THF		500.00
(a) An aliphatic polycarbonate diol, reported to be		
25	polyhexamethylene dicarbonate, available from Stahl USA.	
	(b) Tetrahydrofuran	
	(c) Hydroquinone monomethylether	
	(d) Isocyanatoethylmethacrylate	

30

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Charge 1 was added to an all glass reactor. The ingredients were mixed with an air sparge. Heat was applied to the charge in the reactor until the charge reached a temperature of 60°C. Charge 2 was added over a period of about an hour. Upon completion of the addition of Charge 2, the reaction mixture was mixed for 6 hours. The resulting solution was vacuum stripped at 40°C and 10 mm of mercury for 1 hour. The resulting polymer solution had a measured total solids content, based on the total solution weight, of about 91.71%. The polymer had a weight average molecular weight, as measured by gel permeation chromatography using polystyrene as a standard, of about 6473 and a number average molecular weight of 2480.

15

Component 2Step 1

A polylactone diol bis(chloroformate) intermediate was prepared from the ingredients as summarized in Table 2. The polycaprolactone diol bis(chloroformate) intermediate is useful in the preparation of polycaprolactone diol bis(meth)acryloyl carbonate) monomers.

Table 2		
<u>Ingredients</u>		<u>Weight (grams)</u>
	<u>Charge 1</u>	
phosgene		67
	<u>Charge 2</u>	
polylactone diol (e)		3993
	<u>Charge 3</u>	
phosgene		1713
(e) TONE 0201 poly(epsilon-caprolactone) diol obtained from Union Carbide.		

35

Charge 1 was added over a period of 15 minutes to a 5 liter four-necked round-bottom jacketed flask with concurrent cooling to 5°C. The flask was equipped with a motor driven TEFLON

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polymer stir blade, a phosgene inlet tube, a thermocouple, pressure equalizing addition funnel, and a cold condenser connected to a sodium hydroxide scrubber. With the completion of the addition of Charge 1, Charges 2 and 3 were each added to the flask simultaneously over a period of 8.5 hours and 7.5 hours, respectively. During the addition of Charges 2 and 3, the temperature of the contents of the flask were observed to rise to no more than 38°C. At the end of the addition of Charge 2, a heating mantle was placed on the flask and the contents of the flask were maintained at a temperature of 32°C throughout the rest of the addition of Charge 3. With the completion of the addition of Charge 3, the contents of the flask were sparged at a temperature of 32°C with nitrogen gas for a period of approximately 24 hours. The contents of the flask were transferred to a suitable container. The assay of the reaction was determined to be 99 percent, based on a titration of a mixture of the product and pyridine.

#### Step 2

The polylactone diol bis (chloroformate) intermediate of Step 1 was used with the ingredients summarized in Table 3 to prepare the polylactone diol bis ((meth) acryloyl carbonate) monomer as follows.

Table 3	
<u>Ingredients</u>	<u>Weight (grams)</u>
<u>Charge 1</u>	
polycaprolactone bis(chloroformate) intermediate	328
hydroxyethylmethacrylate	134
methylene chloride	200
<u>Charge 2</u>	
50 percent sodium hydroxide (f)	102
(f) An aqueous solution containing sodium hydroxide in an amount of 50 percent by weight, based on the total weight of the solution.	

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Charge 1 was added to a 1 liter round-bottom jacketed glass flask, which was equipped with a motor driven TEFLON polymer blade, water cooled condenser, a circulating cooling unit (for the 5 jacket of the flask) and a thermometer connected through a temperature feed-back control device. The contents of the flask were cooled to 0°C and Charge 2 was added slowly over a period of 35 minutes. Throughout the addition of Charge 2, the temperature of the contents of the flask was not observed to exceed 20°C.

10 Upon completing the addition of Charge 2, 50 grams of water was added and the contents of the flask were stirred for an additional 2 hours at a temperature of approximately 20°C. The contents of the flask were separated into organic and aqueous phases by the addition of 800 milliliters (ml) of deionized water and 0.05 grams 15 of butylated hydroxytoluene to the flask. The organic phase was collected and washed with 300 grams of a 10 weight percent aqueous sodium hydroxide solution. Deionized water, 400 grams, was added and after 1 hour the organic phase was collected. The organic phase was washed with 500 grams of deionized water containing 20 0.035 grams of butylated hydroxytoluene. The organic phase was collected after 1 hour and washed with 600 grams of deionized water. The organic phase was collected after 18 hours and was sparged with air for 2 hours. The organic phase was stripped at a temperature of 35°C under a vacuum of 12 millimeters (mm) of 25 mercury for 30 minutes and at 48°C under 10 mm of mercury for 40 minutes. The resulting product was filtered through a 0.45 micron filter. The resulting reactive oligomeric product of Component 2 was obtained in 85 percent yield, and was found to have a Hydroxyl number of 5.62mg KOH/gram of sample and a weight average molecular 30 weight, as measured by gel chromatography using polystyrene as a standard, of from 500 to 1400.

### Component 3

The reaction product of a polycarbonate polyol and 35 (meth)acryloyl chloride was prepared from the ingredients as summarized in Table 4.

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Table 4

<u>Ingredients</u>	<u>Weight (grams)</u>
<u>Charge 1</u>	
PC-1122 (a)	234.40
5 THF (b)	301.30
MEHQ (c)	0.24
Sodium acetate	37.40
<u>Charge 2</u>	
10 Methacryloyl chloride	26.2
THF	100.80
(e) An aliphatic polycarbonate diol, reported to be polyhexamethylene bicarbonate, available from Stahl USA.	
(f) Tetrahydrofuran	
15 (g) Hydroquinone monomethylether	

Charge 1 was added to an all glass reactor that had been flushed with nitrogen. The reactor was placed in an ice bath and Charge 2 was added over an interval of 1 hour while maintaining the temperature of the reaction mixture below 25°C. Upon completion of the addition of Charge 2, the reaction mixture was warmed to room temperature over a period of 95 minutes. Heat was applied to the charge in the reactor until the charge reached a temperature of 35°C. Reaction aliquots were quenched with methanol and analyzed by Gas Chromatography for methyl methacrylate to determine reaction conversion. The completed reaction was diluted 1 to 1 in ethyl acetate and washed twice with saturated sodium bicarbonate and twice with brine. The resulting organic solution was dried over magnesium sulfate, filtered and concentrated to approximately 92 percent solids. The resulting material was used without further purification.

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The presence of methyl methacrylate was determined by co-inject with a standard (methyl methacrylate from Aldrich Chemical Company 99%, M5,590-9) on a Hewlett Packard 5890 Series II gas chromatograph containing a Supelco SPB-8 capillary column. A retention time of 4.29 minutes was determined under the following settings; injection port temp 200°C, detector port temp 250°C, column temperature program 2 min hold 40°C, 40-220°C ramp @ 15 deg/min, hold 22 min @ 220°C.

Gel Permeation Chromatography data revealed the following about the final product: Mn is 2400 and Mw is 5600. The GPC system was calibrated with polyethylene glycol standards.

#### Photochromic Component

The Photochromic Component was prepared by adding each of the materials listed in Table 5 to a suitable vessel equipped with an agitator and means for heating. The resulting mixture was agitated and gently heated until a clear solution resulted.

---

Table 5

---

<u>Material</u>	<u>Weight Percent*</u>
NMP (g)	15.000
Photochromic #2 (h)	2.625
Photochromic #3 (i)	0.675
Photochromic #4 (j)	0.900
Photochromic #5 (k)	3.300
Irganox 245 (l)	3.000
Tinuvin 622 (m)	2.000

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\* The weight percents listed in Table 5 are based on the total weight of the monomers.

- (g) N-methylpyrrolidone
- (h) A 2H-naphtho[1,2-b]pyran that exhibits a blue-gray color when irradiated with ultraviolet light.
- (i) A 2H-naphtho[1,2-b]pyran that exhibits a green-blue color when irradiated with ultraviolet light.
- (j) A 2H-naphtho[1,2-b]pyran that exhibits a yellow-orange color when irradiated with ultraviolet light.

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- (k) A 2H-naphtho[1,2-b]pyran that exhibits a yellow-orange color when irradiated with ultraviolet light.
- (l) An antioxidant/stabilizer available from Ciba Specialty Chemicals Corp.
- 5 (m) A hindered amine ultraviolet light stabilizer available from Ciba Specialty Chemicals Corp.

#### Examples 1-14

Table 6 lists the monomers by weight percent in each of  
10 Examples 1-14. The Examples were prepared by adding the monomer composition listed in Table 6 to a suitable vessel equipped with an agitator and mixing for an hour after the following additions: FC-431 fluorocarbon surfactant available from 3M, was added in an amount to provide 0.15 weight percent and Photochromic Component  
15 of Table 5 was added in an amount to provide 28.0 weight percent, both weight percents being based on the total weight of monomers.

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Table 6

Example #	1	2	3	4	5	6	7	8	9	10	11	12	13	14
BPA2EO DMA (n)	45	40	30	45	45	45	70	70	70	70	70	70	70	70
Component 1	35	40	30	8.75	17.5	26.25	30	15	0	15	10	0	0	0
Component 2	0	0	0	26.25	17.5	8.75	0	15	30	0	10	0	0	0
Component 3	0	0	0	0	0	0	0	0	0	15	10	0	0	0
TMPTMA (o)	20	20	20	20	20	20	0	0	0	0	0	0	0	0
BPA 10EO DMA (p)	0	0	20	0	0	0	0	0	0	0	0	30	0	0
BPA 20EO DMA (q)	0	0	0	0	0	0	0	0	0	0	0	0	30	0
BPA 30EO DMA (r)	0	0	0	0	0	0	0	0	0	0	0	0	0	30

(n) Bisphenol A ethoxylated (1 EO/phenyl) dimethacrylate available from Sartomer, Inc.

(o) Trimethylol propane trimethacrylate available from Sartomer, Inc.

(p) Bisphenol A ethoxylated (5 EO/phenyl) dimethacrylate available from Sartomer, Inc.

(q) Bisphenol A ethoxylated (10 EO/phenyl) dimethacrylate available from Sartomer, Inc.

(r) Bisphenol A ethoxylated (15 EO/phenyl) dimethacrylate available from Sartomer, Inc.

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Example 15

The Accelerated Weathering Photochromic Percent Photopic Fatigue Test (AWPPPF Test) comprises preparing lenses in  
5 Parts A-C, coating the lenses with a polymerizable composition in Part D, measuring the Fischer microhardness of the coated lens in Part E, and determining the photochromic performance and fatigue in Part F, before and after weathering in Part G.

The polymerizable composition of the present invention  
10 was incorporated into the coating compositions of Examples 1-8, 10 and 11. Other polymerizable compositions, that did not contain the polymerizable composition of the present invention, such as the compositions of Examples 9, 12, 13 and 14 were also tested. The photochromic performance and fatigue test results for coatings  
15 having comparable Fischer microhardness levels were compared to determine if there was an increase or decrease in these parameters. By comparing coated lenses having comparable Fischer microhardness levels, the physical nature of the coating was taken into consideration, since it is generally known that the  
20 performance of photochromic compounds can be faster in softer polymerized matrices.

Part A

A series of plano lens blanks, prepared from CR-39®  
25 monomer, available from PPG Industries, inc. were used. The lens blanks were 70 mm in diameter. All of the lens blanks were washed with dishwashing detergent (Lemon Scented Joy) and water, immersed in a 12.5 weight percent, based on the total weight of the solution, aqueous sodium hydroxide solution at 60°C for 10 seconds  
30 rinsed with deionized water, sprayed with isopropyl alcohol and dried.

Part B

The lenses prepared in Part A were coated with an  
35 adhesion promoter composition of the type described in U.S. Patent 6,150,430. The adhesion promoter composition was applied to the surface of the lenses by spinning the lenses at 1500 revolutions per minute (rpm) while dispensing the composition for 9 seconds.

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Part C

All of the coated lenses prepared in Part B were cured by exposure to ultraviolet radiation. The lenses were subjected to 5 to 10 seconds of exposure, 6 inches beneath a Dymax 5000EC spot cure system rated at an output of 400 watts per inch. After the applied composition was cured, each lens was rinsed with isopropyl alcohol for 9 seconds while spinning at 1500 rpm, and dried, prior to further processing.

10

Part D

The lenses prepared in Part C were coated with the photochromic coating compositions of Table 6 by spinning the lenses at 1500 rpm and dispensing the coating composition for the time listed in Table 7 to produce a coating having a thickness of approximately 30 microns after curing.

Table 7

20	<u>Example #</u>	<u>Spin Time (seconds)</u>
	1	18.0
	2	25.0
	3	17.0
	4	18.0
25	5	12.0
	6	10.0
	7	35.0
	8	20.0
	9	11.0
30	10	33.0
	11	22.0
	12 and 13	9.0
	14	9.5

35 The coated lenses were cured by exposure to ultraviolet radiation by exposing them on one pass at a speed of 2.3 feet per minute (70.1 cm per minute) on a conveyor belt, beneath two

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ultraviolet type "V" lamps of 10 inch (25.4 cm) length. The first lamp was maintained at a height of 2.5 inches (6.4 cm) above the conveyor and the second lamp at 6.5 inches (16.5 cm) above the conveyor. The curing system was obtained from Eye Ultraviolet 5 system and had been inerted with nitrogen to a level of less than 100 parts per million of oxygen.

#### Part E

The photochromic coated lenses prepared in Part D were 10 subjected to microhardness testing using a Fischerscope HCV, Model H-100 available from Fischer Technology, Inc. The microhardness, measured in Newtons per mm<sup>2</sup>, of the coated lenses of the Examples was determined under the conditions of a 100 milliNewton load, 30 load steps and 0.5 second pauses between load steps. The results 15 reported in Table 8 were measured at an indenter depth of 2um.

Table 8

	<u>Example No.</u>	<u>Microhardness</u> <u>Newtons per mm<sup>2</sup></u>
20	1	100
	2	86
	3	84
	4	117
25	5	112
	6	105
	7	127
	8	127
	9	144
30	10	108
	11	108
	12	189
	13	137
	14	99
35	_____	

The results of Table 8 shows that the Examples 1-8, 10 and 11 containing Component 1 had a microhardness that ranged from

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84 to 108 Newtons/mm<sup>2</sup>. The other examples had a microhardness that ranged from 99 to 189 Newtons/mm<sup>2</sup>.

#### Part F

5           The photochromic coated lenses prepared in Part D were tested for photochromic response on an optical bench made by Essilor of France and is designated the "BMP" hereinafter. Prior to testing on the BMP, the photochromic coated lenses were exposed to 365 nm ultraviolet light for about 10 minutes at a distance of  
10 about 14 cm from the lamps to activate the photochromic compound. The UVA irradiance at the sample was measured with a Licor Model Li-1800 spectroradiometer and found to be 22.2 Watts per square meter. The samples were then placed under a halogen lamp for  
15 bleach, or inactivate, the photochromic compounds in the samples. The illuminance at the sample was measured with the Licor spectroradiometer and found to be 21.9 Klux. The test lenses were then kept in a dark environment for at least 1 hour prior to testing on the BMP.

20           The BMP comprises a flat metal surface to which was fitted two 150 watt Xenon arc lamps positioned 90° apart (one lamp to provide the amount of UV/VIS light and one to provide the additional contribution of visible light). The somewhat collimated output beams from the xenon arc lamps were combined and  
25 directed toward the sample cell and toward irradiance detectors through a 50/50 beam splitter. Each lamp was filtered and shuttered individually and also shuttered after blending, prior to entering the sample cell. Each lamp was also filtered with a Schott 3mm KG-2 band-pass filter. The lamp for supplemental  
30 visible light was additionally filtered with a 400nm cutoff filter.

          The software supplied with the equipment, i.e., BMPSoft version 2.1e, was used to control timing, irradiance, air cell and sample temperature, shuttering, filter selection and response  
35 measurement. The software program provided for adjustments within established set limits to a photofeedback unit, that in turn, made slight adjustments to the lamp wattage and subsequent lamp output. If a selected irradiance could not be achieved within the limits

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of the photofeedback unit, the program indicated the need for a change in selection of neutral density filters for each light path.

Set up of the BMP software required correlation factors  
5 between spectroradiometric measurements at the sample and with a  
Graseby Model 5380 dual channel optometer fitted with a Model  
#268UVA UVA detector and a Model #268P visible light detector.  
The optometer detectors were mounted on an optical rail carrier  
and received one-half of the split and combined light beams from  
10 the xenon arc lamps. The lens sample cell was fitted with a  
quartz window and self-centering sample holder. The temperature  
in the sample cell was controlled at 73.4°F (23°C) through the  
software with a modified Facis, Model FX-10, environment  
simulator. Irradiance at the sample was established at 6.7 Watts  
15 per square meter UVA and 50 Klux illuminance. A Zeiss  
spectrophotometer, Model MCS 501, with fiber optic cables for  
light delivery from a tungsten halogen lamp and through the sample  
was used for response and color measurements. The collimated  
monitoring light beam from the fiber optic cable was maintained  
20 perpendicular to the test sample while passing through the sample  
and directed into a receiving fiber optic cable assembly attached  
to the spectrophotometer. The exact point of placement of the  
sample in the sample cell was where the activating xenon arc beam  
and the monitoring light beam intersected to form two concentric  
25 circles of light. The angle of incidence of the xenon arc beam at  
the sample placement point was  $\approx 20^\circ$  from perpendicular.

Response measurements, in terms of a change in optical  
density ( $\Delta OD$ ) from the unactivated or bleached state to the  
activated or darkened state were determined by establishing the  
30 initial unactivated transmittance, opening the shutter from the  
Xenon lamp(s) and measuring the transmittance through activation  
at selected intervals of time. Change in optical density is  
determined according to the formula:  $\Delta OD = \log(\%T_b/\%T_a)$ , where  $\%T_b$   
is the percent transmittance in the bleached state,  $\%T_a$  is the  
35 percent transmittance in the activated state and the logarithm is  
to the base 10.

The Bleach Rate ( $T_{1/2}$ ) is the time interval in seconds  
for the  $\Delta OD$  of the activated form of the photochromic compound in

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the test square to reach one half the highest  $\Delta OD$  after removal of the source of activating light. The Activation Rate ( $A_{1/2}$ ) is the time interval in seconds of irradiation that it takes to achieve 50% of the change in optical density ( $\Delta OD$ ) obtained after 15 minutes of irradiation. The results for the photochromic coated lenses are listed in Table 9.

Table 9

10	<u>Example #</u>	<u><math>\Delta OD</math> at 15 minutes</u>	<u><math>A_{1/2}(\text{sec})</math></u>	<u><math>T_{1/2}(\text{sec})</math></u>
	1	0.62	18	64
	2	0.63	16	59
	3	0.61	17	63
15	4	0.61	21	86
	5	0.62	20	76
	6	0.59	29	70
	7	0.59	22	87
	8	0.63	25	108
20	9	0.66	28	117
	10	0.58	17	61
	11	0.59	20	75
	12	0.61	79	513
	13	0.66	33	151
25	14	0.66	23	91

The results of Table 9 show that Examples 1-8, 10 and 11 containing Component 1 individually or in combination with Component 2, Component 3, Trimethylolpropane trimethacrylate and/or Bisphenol A (10 ethoxy units) dimethacrylate in a Bisphenol A (2 ethoxy units) dimethacrylate formulation demonstrated Activation ( $A_{1/2}$ ) and/or Bleach ( $T_{1/2}$ ) rates that were faster than all of the other examples tested except Example 14. The change in optical density ( $\Delta OD$ ) of Examples 1-8, 10 and 11 was comparable or somewhat lower than the other Examples tested.

Examination of both Tables 8 and 9 reveals that the Fischer microhardness of the coatings of Examples 1, 4-8, 10 and 11 was equal to or higher than that of Example 14, which indicates

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that the improvement in photochromic performance, e.g., Activation ( $A_{1/2}$ ) and/or Bleach ( $T_{1/2}$ ) rates, demonstrated by Examples 1, 4-8, 10 and 11 was not due to the physical nature of the coating, e.g., being softer or having a lower Fischer microhardness.

5

#### Part G

An ATLAS Ci4000 WEATHEROMETER was used for conducting simulated solar radiation accelerated weathering. The sample results reported in Table 10 were obtained after 65 hours exposure to the filtered Xenon lamp output of 0.25 Watts per square meter at 340 nanometers in the ATLAS Ci4000 WEATHEROMETER. The temperature in the weatherometer was maintained at 45°C and the relative humidity was controlled at 75%. The temperature of the lenses on the black panel holders typically did not exceed 55°C. After the lenses underwent the fatiguing process, they were prepared and measured on the optical bench under the same conditions prior to exposure.

Percent Fatigue (%Fat) was determined by measuring the difference between the change in optical density ( $\Delta OD$ ) of the test sample before and after accelerated weathering and calculating the percent reduction in optical density that the difference represents. Change in optical density ( $\Delta OD$ ) was determined by inserting a test lens in the bleached state into the sample holder, measuring the transmittance ( $T_B$ ), opening the shutter from the Xenon lamp to provide solar simulated radiation to change the test sample from the bleached state to an activated (i.e., darkened) state, measuring the transmittance in the activated state ( $T_A$ ), and calculating the change in optical density according to the formula:  $\Delta OD = \log(T_B/T_A)$  (logarithm is to the base 10). Results may vary by  $\pm 2$ .

The Percent Photopic Fatigue was measured for the wavelength passed by the Photopic filter which closely corresponds to visible light responses detected by the human eye. Results are reported in Table 10.

35

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Table 10

<u>Example No.</u>	<u>% Photopic Fatigue</u>
7	18
8	22
9	26
10	30
11	27
12	28
13	26
14	24

---

5           The results of Table 10 demonstrate that the % Photopic Fatigue of Example 7, containing 30 weight percent of Component 1, was lower than all of the other samples tested. Example 8 which contains 15 weight percent of each of Components 1 and 2 demonstrated a % Photopic Fatigue that was an average of the  
10 results of Examples 7 and 9, which each respectively contain 30% of Component 1 and 30% of Component 2. Example 10 which contains 15 weight percent of Component 1 and 15 weight percent of Component 3, a different polycarbonate polyol based dimethacrylate reaction product than Component 1, demonstrated a % Photopic  
15 Fatigue that was higher than all of the other samples tested. Example 11 which contained 10 weight percent of each of Components 1, 2 and 3 had % Photopic Fatigue results that fell between those of Examples 9 and 10.

          Examples 12, 13 and 14 demonstrated decreasing %  
20 Photopic Fatigue with an increase in the ethoxy units from 10 to 20 to 30 units, respectively.

          Examination of both Tables 9 and 10 demonstrates that photochromic lenses having improved performance, e.g., faster activation and bleach rates, and/or reduced fatigue, e.g., longer  
25 lifetime, were unexpectedly produced utilizing Component 1 alone or in combination with Component 2 and/or Component 3 in a (meth)acrylate formulation in place of Bisphenol A dimethacrylate having 10, 20 or 30 ethoxy units.

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The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as and to the extent that  
5 they are included in the accompanying claims.

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We claim:

1. A photochromic article comprising a substrate and an at least partial coating of an at least partially cured polymerizable composition comprising a photochromic amount of at least one photochromic compound, at least one material comprising at least one carbonate group and at least one hydroxyl group and at least one monoisocyanate containing material having at least one unsaturated group, said photochromic article being adapted to provide a reduction in the percent fatigue of the photochromic compound in an Accelerated Weathering Photochromic Percent Photopic Fatigue Test.
2. The photochromic article of claim 1 wherein the substrate is paper, glass, ceramic, wood, masonry, textile, metal or polymeric organic material.
3. The photochromic article of claim 2 wherein the polymeric organic material is a solid transparent polymer chosen from thermoset or thermoplastic organic polymeric materials.
4. The photochromic article of Claim 1 wherein the substrate is an optical element.
5. The photochromic article of Claim 4 wherein the optical element is a lens.
6. The photochromic article of claim 1 wherein the at least one photochromic compound in the polymerizable composition is chosen from chromenes, spiropyrans, oxazines, mercury dithizonates, fulgides, fulgimides or a mixture thereof.
7. The photochromic article of claim 1 wherein the at least one unsaturated group is chosen from allylic, (meth)acrylic, vinyl or a mixture thereof.
8. The photochromic article of claim 7 wherein the at least one unsaturated group is (meth)acrylic.

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9. The photochromic article of claim 1 wherein the at least one material comprising at least one carbonate group and at least one hydroxyl group is a polycarbonate polyol.

5 10. The photochromic article of claim 1 wherein the polymerizable composition further comprises at least one other copolymerizable monomer.

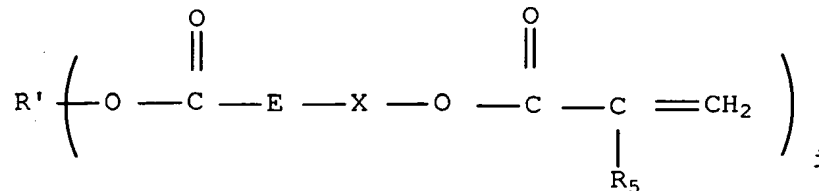
11. The photochromic article of claim 10 wherein the at least one other copolymerizable monomer in the polymerizable composition is a (meth)acrylic monomer.

12. A photochromic article comprising a substrate and an at least partial coating of an at least partially cured polymerizable composition comprising:

- a) a reaction product of a polyol comprising at least one carbonate group and an isocyanate comprising one reactive isocyanate group and at least one polymerizable double bond; and
- 20 b) a photochromic amount of at least one photochromic compound.

13. The photochromic article at claim 12 wherein the at least partial coating of an at least partially cured polymerizable composition further comprises (c) at least one other monomer copolymerizable with component (a).

14. The photochromic article of claim 12 wherein the reaction product (a) of the polymerizable composition is represented by the following formula:



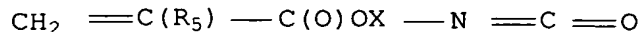
wherein R' is a residue of a polyol comprising at least one carbonate group, R<sub>5</sub> is hydrogen or methyl, E is -NH-; X is a divalent linking chosen from linear or branched chain alkylene,

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linear or branched chain polyoxyalkylene, cyclic alkylene, phenylene, residue of a polyol and C<sub>1</sub>-C<sub>4</sub> alkyl substituted phenylene, and i is chosen from an integer from 2 to 6.

5                    15.    The photochromic article of claim 12 wherein the isocyanate of (a) is chosen from:

(a)    an isocyanate represented by the following formula:



wherein R<sub>5</sub> is hydrogen or methyl and X is a divalent linking  
 10 chosen from linear or branched chain alkylene, linear or branched chain polyoxyalkylene, cyclic alkylene, phenylene, residue of a polyol or C<sub>1</sub>-C<sub>4</sub> alkyl substituted phenylene;

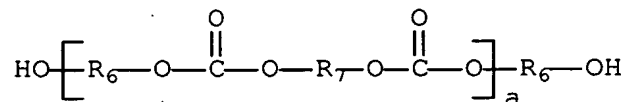
(b)    *m*-isopropenyl- $\alpha$ ,  $\alpha$ -dimethyl benzyl isocyanate;

15                    (c)    a product of the reaction of at least one acrylic functional monomer containing a vinyl ether group and isocyanic acid; or

(d)    a mixture thereof.

20                    16.    The photochromic article of claim 15 wherein the isocyanate is chosen from isocyanatoethylmethacrylate; *m*-isopropenyl- $\alpha$ ,  $\alpha$ -dimethyl benzyl isocyanate; 1-(2-methacryloxyethoxy)ethyl isocyanate; or a mixture thereof.

25                    17.    The photochromic article of claim 12 wherein the polyol comprising at least one carbonate group is a polycarbonate polyol represented by the following formula:



30 wherein R<sub>6</sub> and R<sub>7</sub> are each independently chosen for each occurrence from divalent linear or branched alkylene groups, cyclic alkylene groups or divalent C<sub>6</sub>-C<sub>15</sub> aromatic radicals, and a is an integer selected from 1 to 20.

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18. The photochromic article of claim 17 wherein the polycarbonate polyol is a reaction product of at least one bis(chloroformate) and at least one polyol.

5           19. The photochromic article of claim 18 wherein the bis(chloroformate) is monoethylene glycol bis(chloroformate), diethylene glycol bis(chloroformate), propanediol bis(chloroformate), butanediol bis(chloroformate), hexanediol bis(chloroformate), neopentyldiol bis(chloroformate), bisphenol A  
10 bis(chloroformate) or a mixture thereof.

          20. The photochromic article of claim 18 wherein the polyol is bisphenol A; trimethylolethane; trimethylolpropane; di-  
(trimethylolpropane)dimethylol propionic acid; ethylene glycol;  
15 propylene glycol; 1,3-propanediol; 2,2-dimethyl-1,3-propanediol; 1,2-butanediol; 1,4-butanediol; 1,3-butanediol; 1,5-pentanediol; 2,4-pentanediol; 2,2,4-trimethyl-1,3-pentanediol; 2-methyl-1,3-pentanediol; 2-methyl-1,5-pentanediol; 3-methyl-1,5-pentanediol; 1,6-hexanediol; 2,5-hexanediol; 2-ethyl-1,3-hexanediol; 1,4-  
20 cyclohexanediol; 1,7-heptanediol; 2,4-heptanediol; 1,8-octanediol; 1,9-nonanediol; 1,10-decanediol;; 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate; diethylene glycol; triethylene glycol; tetraethylene glycol; polyethylene glycol; dipropylene glycol; tripropylene glycol; polypropylene glycol; 1,4-  
25 cyclohexanedimethanol; 1,2-bis(hydroxymethyl)cyclohexane; 1,2-bis(hydroxyethyl)cyclohexane; the alkoxylation product of 1 mole of 2,2-bis(4-hydroxyphenyl)propane (i.e., bisphenol-A) and from 2 to 10 moles of ethylene oxide, propylene oxide or a mixture thereof; poly(oxytetramethylene)diol or a mixture thereof.

30

          21. The photochromic article of claim 13 wherein (a) is present from at least 5 percent by weight to less than 95 percent by weight based on the total weight of non-photochromic monomers in the composition.

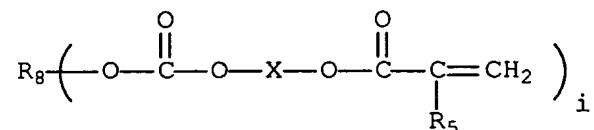
35

          22. The photochromic article of claim 12 wherein reaction product (a) is a monomer having a number average molecular weight greater than 2000.

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23. The photochromic article of claim 13 wherein the at least one other copolymerizable monomer (c) is chosen from:

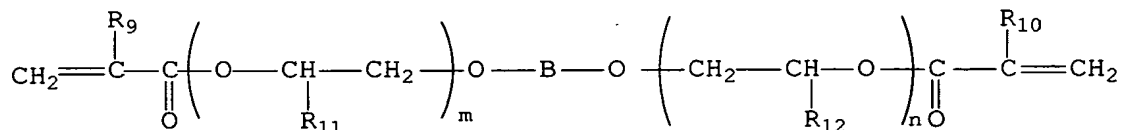
(a) a radically polymerizable monomer  
5 represented by the following formula:



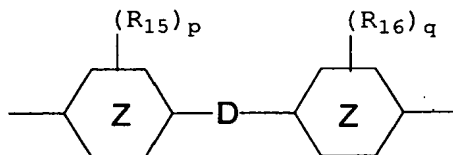
wherein  $R_8$  is a polyvalent residue of a polyol,  $R_5$  is hydrogen or methyl,  $i$  is chosen from an integer from 2 to 6, and X is a divalent linking group chosen from linear or branched chain  
10 alkylene, linear or branched chain polyoxyalkylene, cyclic alkylene, phenylene, residue of a polyol or a  $C_1$ - $C_4$  alkyl substituted phenylene;

(b) a radically polymerizable monomer  
represented by the following formula:

15



wherein  $m$  and  $n$  are each independently chosen from an integer from 0 to 6, the sum of  $m$  and  $n$  being from 0 to 6,  $R_9$  and  $R_{10}$  are each  
20 independently chosen from hydrogen or methyl,  $R_{11}$  and  $R_{12}$  are each independently chosen for each occurrence from hydrogen or  $C_1$  to  $C_2$  alkyl, and B is a divalent linking group chosen from linear or branched chain alkylene, phenylene,  $C_1$ - $C_4$  alkyl substituted phenylene, or a group represented by the following formula:



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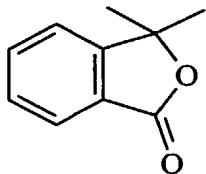
wherein  $R_{15}$  and  $R_{16}$  are each independently chosen for each occurrence from  $C_1$ - $C_4$  alkyl, chlorine or bromine,  $p$  and  $q$  are each



independently chosen from an integer from 0 to 4,

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represents a divalent benzene group or a divalent cyclohexane group and D is -O-, -S-, -S(O<sub>2</sub>)-, -C(O)-, -CH<sub>2</sub>-, -CH=CH-, -C(CH<sub>3</sub>)<sub>2</sub>-, -C(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)- or



when

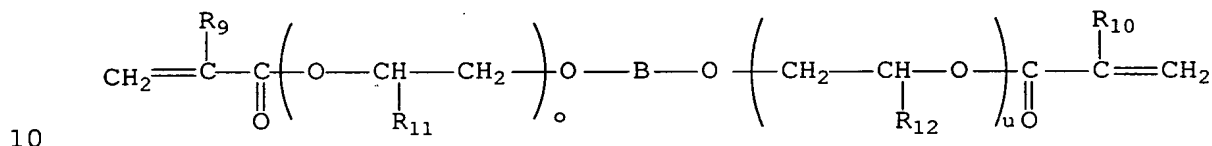


is the divalent benzene group,



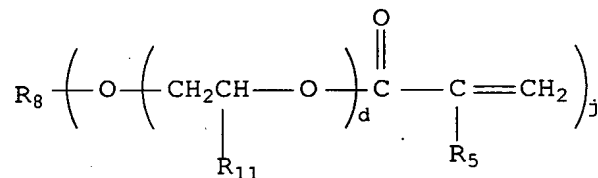
5 and D is -O-, -S-, -CH<sub>2</sub>-, or -C(CH<sub>3</sub>)<sub>2</sub>- when is the divalent cyclohexane group;

(c) a radically polymerizable monomer represented by the following formula:



wherein o and u are each independently chosen from a positive number, the sum of o and u being from 7 to 70, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub> and B are the same as defined hereinbefore;

15 (d) a radically polymerizable monomer represented by the following formula:



wherein R<sub>5</sub>, R<sub>8</sub> and R<sub>11</sub> are the same defined hereinbefore, d is  
20 chosen from an integer from 0 to 20, and j is chosen from a number from 3 to 6;

(e) a reaction product of a polycarbonate polyol polychloroformate and a hydroxy(meth)acrylate;

(f) a reaction product of a polycarbonate polyol  
25 and (meth)acryloyl chloride;

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(g) a radically polymerizable monomer that is monoethylenically unsaturated;

(h) a radically polymerizable monomer that is an allyl functional monomer having at least two allyl groups,  
 5 provided that said allyl functional monomer is used at a level that does not exceed 5 weight percent, based on the total weight of the monomers; or

(i) a mixture thereof.

10 24. The photochromic article of claim 23 wherein:

(a)  $R_8$  being a polyvalent residue of a polyol chosen from an aliphatic polyol, cycloaliphatic polyol, an aromatic polyol or a polyol comprising ester groups containing at least 2 hydroxy groups, i being 2, X being a straight or branched  
 15 chain alkylene;

(b)  $R_9$  and  $R_{10}$  each being methyl,  $R_{11}$  and  $R_{12}$  each being hydrogen, p, q, r and s each being 0, D being  $-C(CH_3)_2-$  and the sum of m and n being from 0 to 4;

(c) the sum of o and u being from 10 to 30;

20 (d)  $R_8$  being a residue of trimethylolpropane, pentaerythritol or dipentaerythritol and d being from 3 to 15;

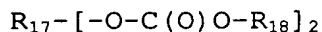
(e) the reaction product of a polycarbonate polyol polychloroformate and;

(f) the reaction product of a polycarbonate  
 25 polyol and methacryloyl chloride;

(g) the monoethylenically unsaturated monomer being an alkyl ester of (meth)acrylic acid, vinyl aromatic monomer, vinyl halide, vinylidene halide, vinyl ester, (meth)acrylic acid or a mixture thereof;

30 (h) the allyl functional monomer being:

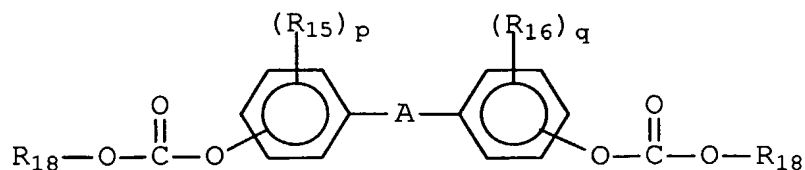
(i) an allyl functional monomer represented by the following formula,



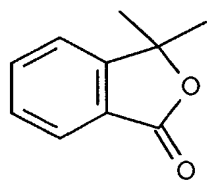
wherein  $R_{17}$  being a divalent residue of a diol chosen from 1,2-  
 35 ethane diol diethylene glycol or 1,2-propane diol, and  $R_{18}$  being an allyl group;

(ii) an allyl functional monomer represented by the following formula,

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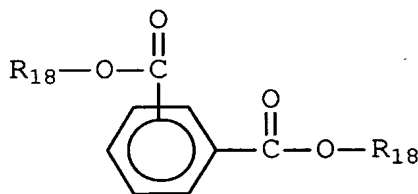


wherein  $R_{15}$  and  $R_{16}$  each being independently chosen for each occurrence from  $C_1$ - $C_4$  alkyl, chlorine or bromine,  $p$  and  $q$  each being independently chosen from an integer from 0 to 4, and  $-A-$  being a divalent linking group chosen from  $-O-$ ,  $-S-$ ,  $-S(O_2)-$ ,  $-C(O)-$ ,  $-CH_2-$ ,  $-CH=CH-$ ,  $-C(CH_3)_2-$ ,  $-C(CH_3)(C_6H_5)-$



or , and  $R_{18}$  being an allyl group;

(iii) an allyl functional monomer represented by the following formula,



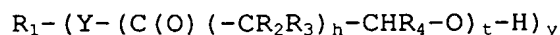
10

wherein  $R_{18}$  being an allyl group; or

(iv) a mixture at least two of (i), (ii) and (iii).

15

25. The photochromic article of claim 23 (a) wherein  $R_8$  being the residue of a polyol represented by the following formula:



20

wherein:  $Y$  is  $-O-$  or  $-NR-$  and  $R$  is hydrogen or  $C_1$ - $C_{12}$  alkyl;  $R_1$  is an organic radical derived from an initiator,  $R_2$ ,  $R_3$  and  $R_4$  are each selected independently for each occurrence from hydrogen,  $C_1$ - $C_{12}$  alkyl,  $C_5$ - $C_6$  cycloalkyl,  $C_1$ - $C_6$  alkoxy, benzyl or phenyl, provided that at least  $h+2$  of the total number of  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen, letter  $h$  is chosen from an integer from 1 to 6;  $t$  is

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chosen from an integer from 1 to 100; and y is chosen from an integer equal to from 2 to 6.

26. The photochromic article of claim 23 (a) wherein  
5 R<sub>8</sub> being the residue of a reaction product of at least one diol  
and at least one lactone; said diol being a linear or branched  
aliphatic diol having from 2 to 20 carbon atoms, poly(C<sub>2</sub>-  
C<sub>4</sub>)alkylene glycol, cycloaliphatic diol having from 5 to 8 carbon  
atoms in the cyclic ring, monocyclic aromatic diol, bisphenol,  
10 hydrogenated bisphenol or a mixture thereof; said lactone being:  
beta-propiolactone; gamma-butyrolactone; beta-butyrolactone;  
delta-valerolactone; alpha-methyl-gamma-butyrolactone; beta-  
methyl-gamma-butyrolactone; gamma-valerolactone; epsilon-  
caprolactone; monomethyl-epsilon-caprolactones;, monoethyl-  
15 epsilon-caprolactones; monopropyl- epsilon-caprolactones;  
monododecyl epsilon-caprolactones; methoxy epsilon-caprolactones;  
ethoxy epsilon-caprolactones; cyclohexyl epsilon-caprolactones;  
phenyl epsilon-caprolactones; benzyl epsilon-caprolactones; zeta-  
enatholactone; eta-caprylactone or a mixture thereof.

20

27. The photochromic article of claim 12 wherein the  
substrate is paper, glass, ceramic, wood, masonry, textile, metal  
or polymeric organic material.

25 28. The photochromic article of claim 27 wherein the  
polymeric organic material is a solid transparent polymer chosen  
from thermoset or thermoplastic organic polymeric materials.

29. The photochromic article of Claim 28 wherein the  
30 substrate is an optical element.

30. The photochromic article of Claim 29 wherein the  
optical element is a lens.

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31. The photochromic article of Claim 12 further comprising a primer interposed between the substrate and the at least partial coating of an at least partially cured polymerizable  
5 composition.

32. The photochromic article of Claim 31 further comprising a protective coating applied to the surface of the at least partial coating of an at least partially cured polymerizable  
10 composition.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/35063

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D5/00 C09K9/02 G02B1/04 G02B1/10 G02B5/23

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C09K G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 025 026 A (SMITH ROBERT A ET AL) 15 February 2000 (2000-02-15) * the entire document *	1-32
A	WO 00 78832 A (PPG IND OHIO INC) 28 December 2000 (2000-12-28) * the entire document *	1-32
A	US 5 965 680 A (PARKHE AJAY D ET AL) 12 October 1999 (1999-10-12) * the entire document *	1-32
A	US 5 973 093 A (CRANO JOHN C ET AL) 26 October 1999 (1999-10-26) * the entire document *	1-32
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 February 2003

Date of mailing of the international search report

24/02/2003

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# INTERNATIONAL SEARCH REPORT

Internati pplication No  
PCT/us 02/35063

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 6 083 427 A (HENRY DAVID)  4 July 2000 (2000-07-04)  * the entire document *</p> <p style="text-align: center;">-----</p>	1-32

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Information on patent family members

International Application No

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